Computational screening of organic molecules for use in batteries

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Glossary

B3LYP The Becke, 3-parameter, Lee-Yang-Parr hybrid functional

C-PCM the conductor-like polarisable continuum model

CI configuration interaction

HF Hartree-Fock

HOMO highest occupied molecular orbital

LUMO lowest unoccupied molecular orbital

MP2 second-order Møller-Plesset perturbation theory

MV methyl viologen

PV photovoltaic

RFB redox flow battery

RO restricted open-shell

SHE standard hydrogen electrode

TEMPO 2,2,6,6-tetramethylpiperidin-1-oxyl

ZPE zero-point vibrational energy

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Acknowledgements

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Abstract

Reliable energy storage is a significant obstacle for achieving independence from non-renewable energy sources. Cheap, environmentally benign and high-capacity batteries are required. This thesis focusses on computational design of novel organic molecules for use in next-generation battery technologies. A computational protocol is benchmarked to reliably determine the energy profiles for organic molecules undergoing redox reactions, and applied to substituted quinones and organic radical species to determine recharging energy barriers and total energy stored. Pairs of redox couples were identified to achieve maximum energy storage and therefore high voltages, and with optimal energy barriers for photorechargeability. This work will inform chemical synthesis and electrochemical experiments in pursuit of high-performing fully organic batteries.

Chapter 1

Introduction

1.1 The energy crisis and the storage problem

Electrical grid networks face fluctuating demand levels and minimal storage facilities; the amount of electricity generated must be flexible to meet consumer demand at any given time. Due to the lack of storage capability and some uncertainty in predicting demand, electrical power production must be greater than electrical power use at all times. This poses a significant problem for the development of renewable energy sources, as many of these (e.g. wind and solar power) have power outputs that do not match demand.[1] For example, solar power cannot be generated overnight, yet power demand peaks in the evening and early morning.[2] The ability to store electrical energy as it is generated would decouple supply from demand, and make 100% renewable electricity generation a feasible prospect.

Solar radiation is a particularly promising source of renewable energy due to its high power density; the amount of energy used by humans in one year is radiated onto Earth's surface in one hour.[3,4] There has been much recent research toward long-term storage of solar energy, via photoelectric synthesis of H_2 or simple organic compounds, pumped-hydroelectric storage, and in novel battery designs.[5,6]

1.2 Redox flow batteries

Redox flow batteries (RFBs) could be a promising option for directly storing solar energy because they consist of redox-tunable components and have long working lifespans. RFBs comprise solutions of electrochemically active species pumped past electrodes, which means that no phase change occurs in their charging or discharging. During charging, electrical energy is converted into chemical potential energy by driving an endergonic (non-spontaneous) redox reaction, then storing the electrolyte. To discharge, charged electrolyte is pumped to electrodes where an electrical device is connected, and electrical energy is released through a spontaneous redox reaction. A schematic diagram of a RFB is illustrated in Figure 1.1.

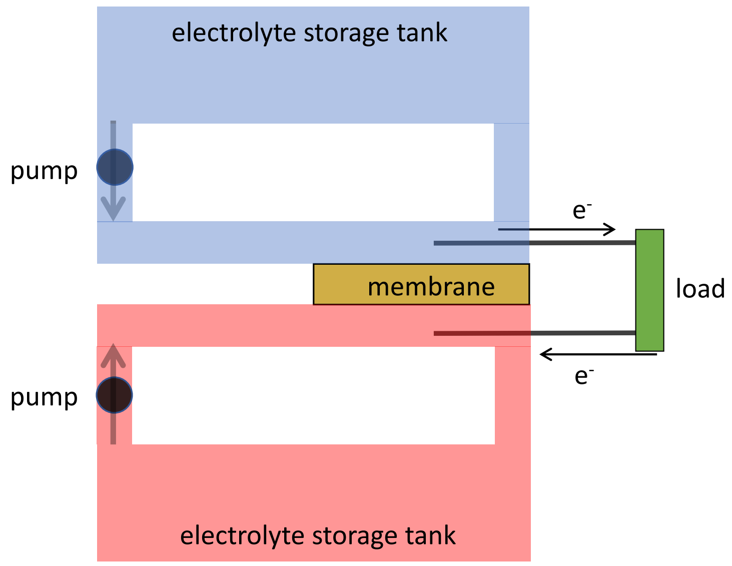


Figure 1.1: Redox flow battery schematic diagram; the two tanks contain different electrolytes which are pumped to the membrane to release electrical energy through a redox reaction.

Since the electrodes do not act as reactants, as they do in conventional batteries, degradation of electrodes is much slower, which significantly increases the lifetime of the battery. The separated liquid components allow for larger RFBs with higher electrical capacities to be safely built than traditional battery schemes would allow. Furthermore, the electrical capacity of a RFB (determined by the amount of energy-storing chemical species present) is independent of its power (determined by the surface area of the electrodes) due to the redox-inactive electrodes. Therefore a RFB can be constructed for particular capacity and power needs. However the voltage (energy stored per electron transfer) is inherent to the redox chemical reaction that occurs between the electrolytes. In order to be useful in a wide range of applications, the voltage of a battery needs to be high.

Another practical consideration in the development of RFBs as devices for electrical energy storage is cost. Grid storage is currently reasonably uncommon due to the high costs involved.[4] Current-generation RFBs and traditional batteries use inorganic redox-active species and precious metal-containing electrode surfaces.[1] These are often expensive and challenging components to work with, and also present personal and environmental safety hazards. Lithium is a element which is scarce and expensive due to its low concentrations in natural supplies, and demand for lithium is expected to increase.[7] The use and disposal of heavy metals has resulted in high pollution levels in water sources around the world. High levels of heavy metals including lead, nickel and cadmium are toxic to human and aquatic life.[8,9] A decreased dependence on such elements is necessary for a secure and stable energy supply in the future. However, many existing alternative technologies fall short of United States Department of Energy targets for gravimetric and volumetric power densities (2.0 kW kg^{-1} and 2.5 kW L^{-1}) and battery longevity (5,000 hours).[10] A battery built with cheaper materials, such as organic electrolytes and carbon electrodes, could overcome both of these issues.

1.3 Quinones

Quinones (Figure 1.2) are good candidates as redox-active components of organic batteries, as they can undergo reversible redox reactions,[11] with high and tunable redox potentials.[12]

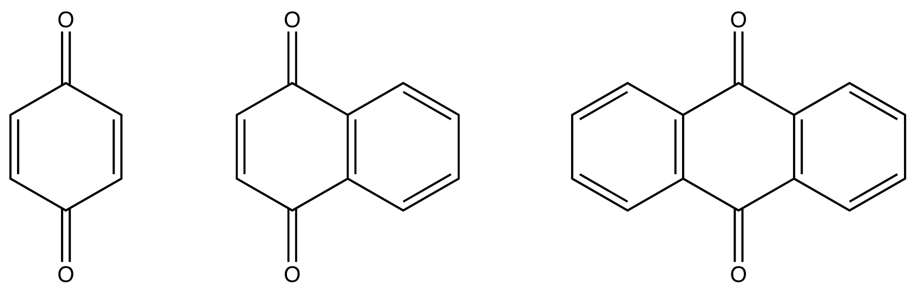


Figure 1.2: Benzoquinone, naphthoquinone and anthraquinone (L–R) can each be reduced to hydroquinones as in Figure 1.3.

They are also chemically stable, and have long been studied for their electrochemical properties; they are reduced by two electrons to hydroquinones. The conjugated system of a quinone allows for reversible electron transfer to and from the molecule, making it an excellent choice as an electrolyte in a RFB. Under medium pH conditions, quinones undergo two one-electron reductions, each followed by a protonation step (Figure 1.3).[13]

p-Benzoquinone is a useful scaffold for synthesis; it undergoes facile nucleophilic conjugate addition and subsequent oxidation that can give mono-, di-, tri- and tetrasubstituted products;[14,15] however,

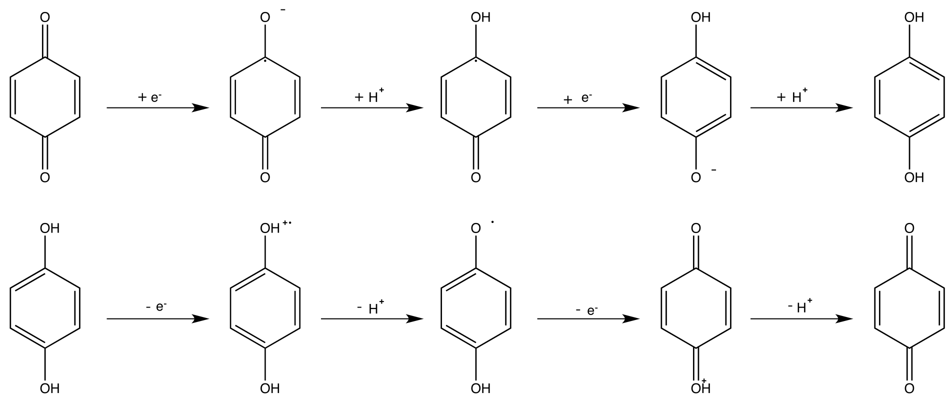


Figure 1.3: In neutral protic media 1,4-benzoquinone, the simplest quinone, undergoes reduction (top) and oxidation (bottom) by an eHeH mechanism.

the synthetic conditions can be controlled to give a good yield of monosubstituted product.[16] In the hydroquinone form, molecules may undergo electrophilic aromatic substitution.[17] This makes *p*-benzoquinones good candidates for RFB components as their redox chemistry can be tuned by the choice of substituted groups; both nucleophiles and electrophiles may be substituted. The effect of substituents on the redox potential of a quinone couple is well-studied. Electron-donating and electron-withdrawing groups decrease and increase the reduction potential of a quinone, respectively.[12,18] Derivatives of larger quinones—naphthoquinone, anthraquinone and phenanthrenequinone—also have potential to be useful battery components.[19] The additional conjugated rings can be viewed as substituents that allow further electron delocalisation, and decrease the reduction potential.[20] Quinone-based RFBs have been reported which use carbon electrodes, avoiding the need for expensive precious metal electrodes.[19,21]

Modifying quinones by adding chemically interesting substituents can alter the electrochemical potential of oxidation and reduction. However, the potential range of substituents and substitution patterns is so large that direct experimental synthesis and characterisation would be prohibitive. Therefore, computationally screening a large number of substituted quinones to provide information to direct synthesis is useful. Identifying substitution patterns which have potential for energy storage can reduce time wasted synthesising molecules which do not store significant amounts of energy. In 2015, Er reported results of computationally screening singly- and fully-substituted quinone/hydroquinone couples.[12] It was found that substitution patterns had a significant effect on electronic and solvation energies. However, only total energy stored (the two-electron, two-proton redox energy) was calculated, with no investigation of the energies of intermediate species. Furthermore, species which are more than singly-substituted but not fully-substituted were not included. Most of the fully-substituted species are unlikely to be chemically viable due to high degrees of steric crowding. This is evidenced by the fact that quinone-based RFBs to date have had limited substitution. Where more substituted quinones have been studied for use in RFBs, their substitutions have been made with polar groups like sulfonate and hydroxyl groups for the purpose of solubility in aqueous systems, rather than for explicitly tuning the thermodynamics of their reactions. Although significant experimental research has been undertaken in constructing RFBs with quinones, they have generally been paired with inorganic redox couples such as bromine/bromide or ferricyanide to provide a high redox potential difference.[19,22] An aqueous RFB comprising quinone/hydroquinone and iodine/iodide half-cells has been reported to have a pH-dependent voltage of 0.28–0.73 V, which is insufficient for practical use.[23] Work by Wedege noted that the biggest challenge for the development of all-quinone battery technology is their generally low voltage, and that functional group substitution could be a way forward.[24]

1.4 Persistent organic radicals

Radical chemical species have one or more electrons which are not spin-paired. Most organic radicals are unstable, transient intermediates in chemical reactions, although some are stable enough to observe directly or isolate.[25] Some functional groups such as the aminoxyl group have well-known redox properties, undergoing a one-electron oxidation to the oxoammonium group (Figure 1.4).

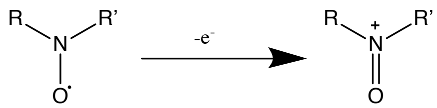


Figure 1.4: Aminoxyl radicals (left) undergo one-electron oxidations to oxoammonium cations

There is a strong chemical driving force for radical species to undergo one-electron redox reactions to form closed-shell species, although this is somewhat offset by the fact that they concurrently form charged species. The balance of energy between the two redox forms can be readily tuned by changing the solvent environment, as polar solvents stabilise charged species more than neutral species. However, the solvent must be of a polarity that can dissolve the molecule in both redox states. Furthermore, functional group substitution of the radical species can change the relative energies of the radical/ion pair. Electron-donating groups lower the energy of forming dications, while electron-withdrawing groups lower the energy of forming anions. Both electron-donating and electron-withdrawing groups stabilise radicals. In fact, the particularly high stability of a radical due to the synergy of nearby electron-donating and electron-withdrawing groups is well-known (captodative effect).[26] Other persistent organic radical species include heterocycles with trivalent nitrogen atoms, cyclopentadienyl radicals and phenoxyl radicals.[25]

Organic electrodes based on polymers containing aminoxyl radicals are well-studied, and their practical use in batteries was described in 2011 as being “near at hand”.[27] Li reported a non-aqueous battery with organic electrolytes 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and N-methylphthalimide.[28] More recently, an aqueous organic battery comprising the organic radical electrolytes methyl viologen (MV) and TEMPO has been reported with a voltage of 1.25 V.[29]

1.5 Photorecharging

Organic redox reactions often have the disadvantage of having lower cell potentials (voltages) than inorganic reactions. To utilise organic redox chemistry in batteries, the energy stored must be high to compete with existing inorganic technologies. In general, power supply is from high-voltage sources so maximising battery voltages to match them minimises energy losses upon charging. However, the lower redox potentials and high tunability of redox-active organic molecules can be turned into an advantage by using them in conjunction with low-voltage power supplies, like direct current produced photovoltaically or direct charging from a photovoltaic electrode. Designing and developing such a photorechargeable battery is the key strategy proposed in this thesis. To this end, electrolytes must be designed to enable recharging directly from solar energy to minimise energy losses. A conceptual diagram of a photorechargeable RFB is illustrated in Figure 1.5. It comprises a conventional RFB (two cells on left) coupled to a photorecharging unit (cell on right).

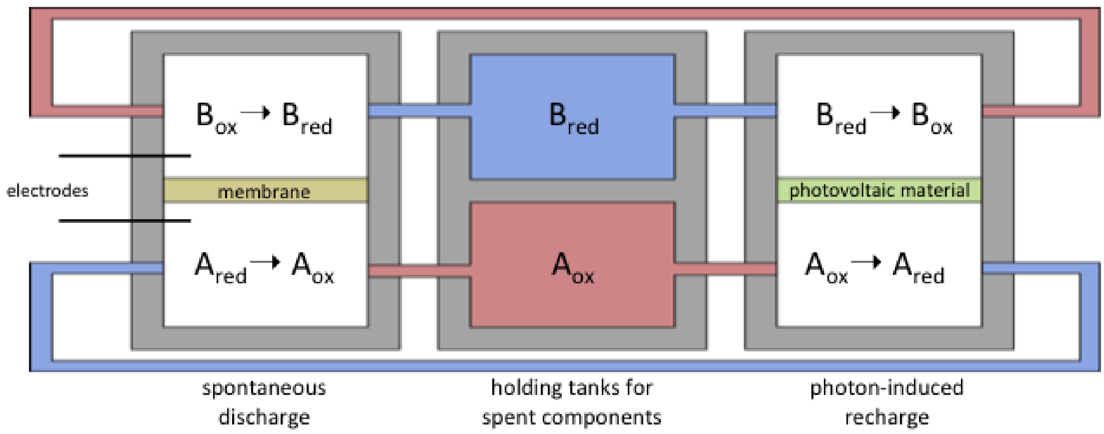


Figure 1.5: Schematic for a photorechargeable RFB. Discharge at the left end releases electrical energy when the circuit is completed at the electrodes by a device. At the right end, electrical energy is produced by photons interacting with the PV material drives the charging reaction

In a fully organic *photorechargeable* RFB, proposed in this thesis, the endergonic charging step(s) must be accomplished photovoltaically. Therefore, the redox potentials for the photorecharging processes must be tuned to match the available energy which is determined by the photon energy of the incident radiation and band gap of the PV material. A fully organic photorechargeable battery would be environmentally benign both in construction materials and in its solar energy source.

To determine photorecharging efficiency, the energy of incident photons from solar radiation and their abundance must be considered. The Shockley–Queisser limit is the maximum efficiency for conversion of light energy to useful potential energy of a solar cell comprising a single charge separator.[30] Using experimental data from the ASTM G-173 standard AM1.5G spectrum, this limit is calculated to be 33.7% for the most efficient band gap of 1.3 eV (130 kJ mol^{-1}, 950 nm) (Figure 1.6).[31]

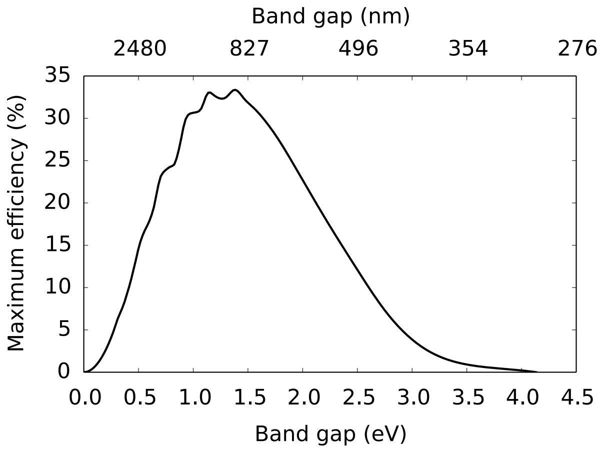


Figure 1.6: The Shockley–Queisser limit shows maximum solar energy-capturing efficiency at band gaps around 0.8–2.0 eV (80–190 kJ mol^{-1}).

Cell efficiency is above 25% for band gaps of 0.8–2.0 eV (80–190 kJ mol^{-1}), corresponding to light in the visible and near-infrared regions. Therefore, for a photorechargeable battery to be practicable, it must be charged by photons of these energies.

1.6 Aims

The aim of this thesis is to use quantum chemical methods to model redox chemistry in organic molecules and optimise the redox potentials of promising redox-active battery components for use in electrically rechargeable and photorechargeable RFBs. Firstly, a method for accurate modelling of redox energies in organic molecules will be established and benchmarked. This method will be applied to a range of substituted quinones of different sizes to find those optimally suited for use in photorechargeable RFBs. The redox potentials of known stable radical organic species and a selection of substituted derivatives will be computed to determine promising redox pairs for use in electrically or photochemically rechargeable RFBs.

Chapter 2

Benchmarking

2.1 Introduction

In order for quantum chemical calculations to be useful in designing novel organic redox components, they must be accurate enough that the results are chemically meaningful but fast enough that a large number of species can be studied. To achieve the optimal balance between computational efficiency and accuracy, it is useful to benchmark faster, more approximate models against higher-level methods that will be more accurate but take longer to run.

The level of quantum theory and the size of the basis set used in a quantum chemical calculation determines the quality of the calculated wavefunction and electronic gas-phase energy. Both the electronic structure method and the size of the basis set must be selected carefully to ensure an appropriate balance between accuracy and time cost. The more flexibility in the atomic orbitals used (larger basis set) and the more comprehensively electron correlation is calculated (level of theory), the higher the quality the calculation is, but the more computationally intensive it is. This is illustrated in the Pople diagram (Figure 2.1) below.

Different families of basis sets comprise different numbers of contracted Gaussian basis functions for each atomic orbital. Increasing the size of a basis set from single-zeta to triple-zeta increases the number of basis functions that describe the valence shell of each atomic orbital from one to three. The computational time required increases as a function of the number of basis functions, depending on the method used. Moving along the x-axis, Hartree-Fock (HF) is the most approximate electronic structure model but also the fastest to evaluate, while configuration interaction (CI) models are

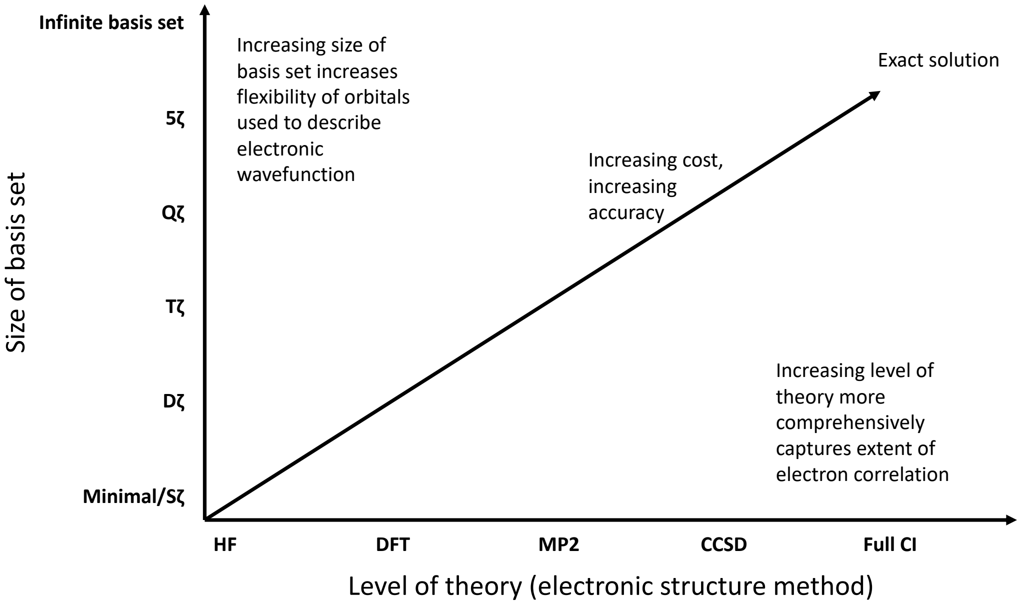


Figure 2.1: The quality of a quantum chemical calculation increases with the extent to which electron correlation is captured (horizontal axis) and with increasing basis set (vertical axis). HF = Hartree-Fock; DFT = density functional theory; MP2 = second-order Møller-Plesset perturbation theory; CCSD = coupled-cluster, singles and doubles; CI = configuration interaction

more realistic but also take substantially longer. Full CI in an infinite basis set provides the exact solution to the Schrödinger equation. However, such a calculation would take an infinitely long time to complete. At the other extreme, a calculation using a low-quality method in a small basis set will be fast but not accurate. Moving along the diagonal between these two extremes is a sensible strategy, where the errors due to basis set incompleteness and treatment of electron correlation are approximately balanced.

The change in free energy is the thermodynamic quantity which governs chemical reactivity and is stored and lost in chemical reactions. It is related to changes in enthalpy and entropy as shown in Equation 2.1:

$$\Delta G = \Delta H - T\Delta S \tag{2.1}$$

where ΔG is change in Gibbs free energy, ΔH is change in enthalpy, T is temperature and ΔS is change in entropy. Gas-phase enthalpy is made up of electronic, translational, rotational and vibrational components. In particular, vibrational enthalpy can be significant due to zero-point vibrational energy (ZPE). Solvation also effects the enthalpy of a chemical system. Entropy comprises translational, rotational and vibrational disorder. Equation 2.1 can be rewritten:

$$\Delta G = \Delta H_{\text{electronic}} + \Delta H_{\text{vibrational}} + \Delta H_{\text{solvation}} - T(\Delta S_{\text{solute}} + \Delta S_{\text{solvation}}) \tag{2.2}$$

Electronic enthalpy values are determined by standard single-point energy quantum chemical calculations. Vibrational enthalpy and solute entropy values require frequency calculations to be performed, which involve determining second-order derivatives of electronic energy with respect to nuclear coordinates. This is a computationally intensive process, and the increased accuracy of free energy values provided by performing frequency calculations must be weighed up against the increased cost. Solvation stabilisation enthalpies and entropies are especially important for dipolar and electrically charged molecules. Explicitly modelling solvent molecules requires shells of individual solvent molecules to be modelled and different conformational arrangements to be sampled, often using molecular mechanics or Monte Carlo simulations. Implicit solvation models forgo solvent molecules for a sphere of dielectric so that the solvent environment is averaged out across the entire solute surface.[32] Continuum solvation models have been shown to calculate the qualitatively correct solvation energies for a range of organic radical species.[33]

This thesis is based on using quantum chemical calculations to inform the design of novel organic energy storage components for photorechargeable redox flow batteries using quantum chemical calculations to inform the design. The aim of this chapter is to quantify errors associated with using different electronic structure methods, basis sets and solvation models to establish a reliable and cost-effective computational protocol for calculating the barrier heights and energy stored for redox charging reactions. The importance of the different contributions to ΔG will be determined. Appropriate computational methods will be established to calculate each value while optimally balancing accuracy and computational cost. Approximations made may compromise the exactness of the term free energy, so the sake of simplicity, changes in energy will be referred to as ΔE values unless specifically defined as changes in free energy or enthalpy. Benchmarking will be performed using a prototype reaction.

In this chapter the energy-storing reaction of benzohydroquinone and anthraquinone to produce benzoquinone and anthrahydroquinone is used as a case study to construct a computational protocol which will later be extended to substituted quinones and persistent radical organic species. The reaction mechanism must be elucidated in order to map out reaction coordinate diagrams.

2.2 Recharging mechanism

Energy is stored in a battery by transferring electrons during a pair of coupled redox half-reactions from lower- to higher-energy electronic states. The difference in energy between these two states is the amount stored which can be used when required as electrical energy. For each half-reaction in an all-quinone battery, two electrons are transferred to convert quinones to hydroquinones, and vice versa. In a protic environment, two protons are also transferred, which decreases the amount of energy stored. For example, if anthraquinone is reduced by gaining two electrons and two protons, and benzohydroquinone is oxidised by losing two electrons and two protons, energy is stored. The mechanism for this charging redox reaction is shown in Figure 2.2.

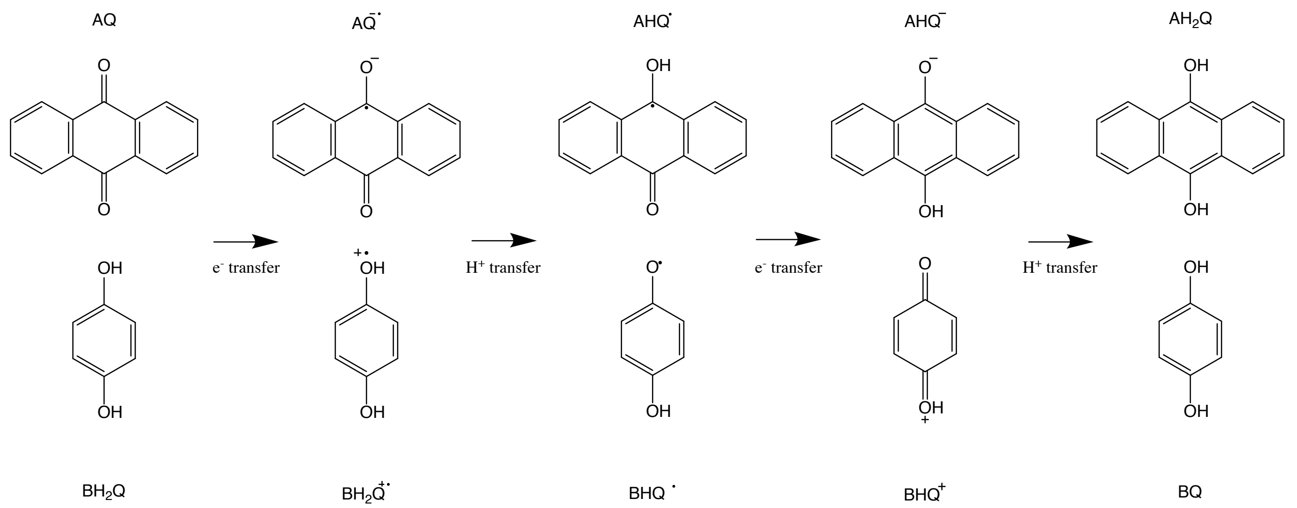


Figure 2.2: Reaction mechanism for the reduction of anthraquinone and oxidation of benzohydroquinone. This is a charging reaction – energy is stored. The reverse reaction occurs to release stored energy when needed.

The overall result of the two electron-transfer steps and two proton-transfer steps is that two electrons have been transferred from a lower-energy orbital in benzohydroquinone to a higher-energy orbital in anthraquinone (Figure 2.3). This energy can be released in a battery when needed, as the reverse reaction is exothermic and spontaneous. The first objective of this work is to reliably determine the amount of energy stored by the benzohydroquinone–anthraquinone charging reaction.

The second objective is to determine the barrier heights for each step in the recharging process, as illustrated in Figure 2.4.

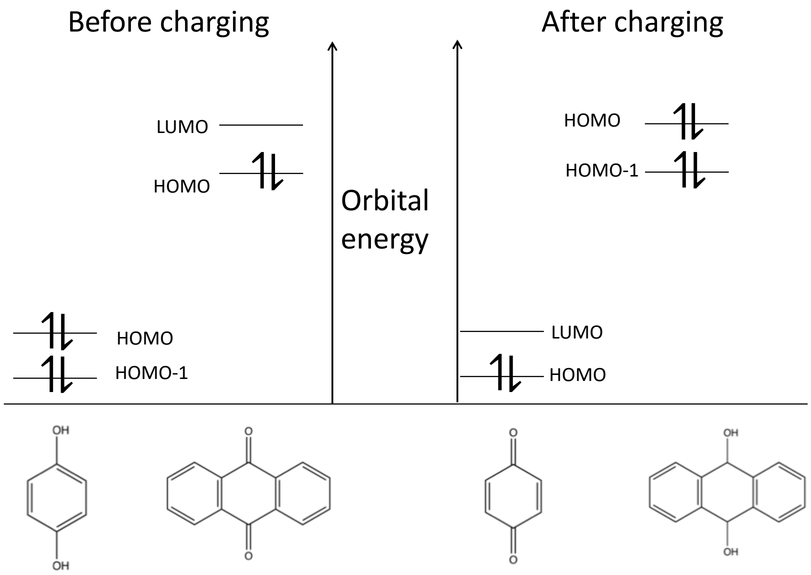


Figure 2.3: After the charging reaction, two electrons have been transferred from the HOMO of the benzohydroquinone to the LUMO of the anthraquinone to give benzoquinone and anthrahydroquinone. Since the electrons have moved from a lower-energy orbital to a higher-energy orbital, energy is stored.

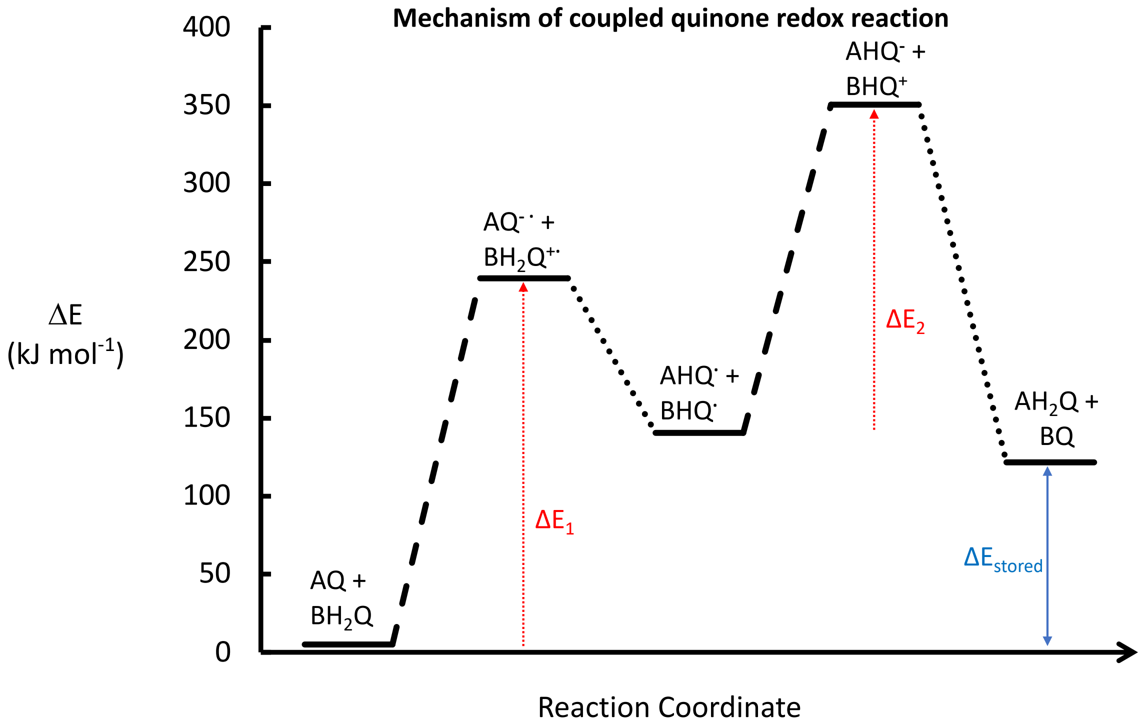


Figure 2.4: Reaction energy profile for the reduction of *p*-anthraquinone (AQ) and oxidation of *p*-benzohydroquinone (BH_2Q). Dashed lines represent electron transfer steps and dotted lines represent proton exchange steps. To create a photorechargeable battery, the energy barriers (ΔE_1 and ΔE_2) should be lowered, and the total energy stored (ΔE_{stored}) should be maximised.

2.3 Computational methods

The reaction coordinate diagram was constructed by calculating the sum of the energies of the two species at each step of the mechanism (Figure 2.2). The relative energies of ΔE_1, ΔE_2 and ΔE_{stored}

were then determined by taking appropriate differences. All calculations were carried out using the Q-Chem 4 quantum chemistry program package.[34]

Molecular geometries were optimised using B3LYP.[35,36]/6-311G(d).[37] MP2 and B3LYP methods were used to determine the electronic energies of the quinone species. For radical species, restricted open-shell (RO) MP2 was used rather than unrestricted MP2 due to the high spin contamination in UHF wavefunctions. For unrestricted methods such as B3LYP, spin contamination is generally not significant.[38] ROMP2 is more resource-intensive than UMP2 and much more intensive than B3LYP. The most appropriate electronic structure model will be selected to provide reliable results without very expensive calculations. The effect that basis set size has on the reliability of geometry optimisation and single-point energy calculations was explored, by comparing results of calculations from a range of triple-zeta Pople basis sets with and without diffuse functions, and with different polarisation functions. The importance of ZPE and gas-phase entropy was tested by performing frequency analysis calculations using B3LYP. Implicit solvation modelling with the the conductor-like polarisable continuum model (C-PCM)[39–41] was examined, using dielectric constants (ε) of 2, 5, 10 and 20.

2.4 Results and discussion

2.4.1 Basis set effect on optimised geometries

Geometry optimisations were performed using B3LYP at 6-311G, 6-311G(d) and 6-311+G(d).[37,42] B3LYP is an appropriate method for geometry optimisations for this work. Geometries of organic molecules generally do not vary much when optimised with different quantum chemical methods. B3LYP in particular is a cost-effective method, and has been known to attain better agreement with experimental geometries than HF MP2, and other methods.[43] Single-point energy calculations were performed on these geometries at MP2/6-311+G(d,p). The calculated energy for each species is the same across the different geometry optimisation basis sets, except for the benzosemiquinone radical ($BHQ^{\bullet}$), which is identical for the geometries calculated in 6-311G(d) and 6-311+G(d) but not 6-311G. The basis set used for geometry optimisations will therefore be 6-311G(d), as it performs as well as 6-311+G(d) but is slightly smaller and therefore less computationally intensive.

2.4.2 Electronic structure model ($\Delta H_{\mathrm{electronic}}$)

Single-point energy calculations were carried out for all ten species involved in the unsubstituted charging reaction using MP2 and B3LYP at 6-311+G(2d,p).[37,42,44] Results are shown in Figure 2.5.

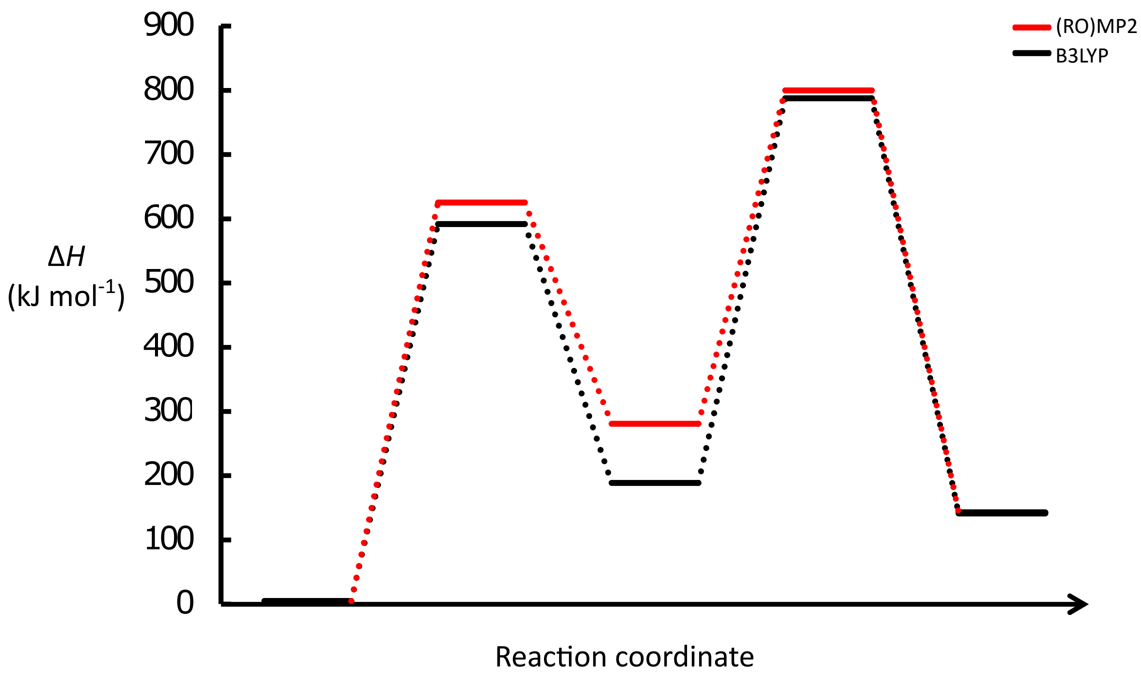


Figure 2.5: Reaction energy profile for the reduction of p-anthraquinone (AQ) and oxidation of p-benzohydroquinone (BH_2Q). B3LYP agrees closely with (RO)MP2 except for radical species.

Relative energies (fixing the energy of reactants at zero) calculated using MP2 and B3LYP closely agreed with each other at steps 4 and 5, where all species are singlet. At steps 2 and 3, where radical species are present, ROMP2 and B3LYP results differed most. There is an approximately 10% error for the calculated values of ΔE_1 and ΔE_2 due to the use of DFT, but this is acceptable given the improved performance of DFT. The calculated values of $\Delta E_{\mathrm{stored}}$ are very similar between the two methods; the error for this value is only 2%. These uncertainties should be applied to calculated energy barrier heights and stored energies for the rest of the thesis. The cost of DFT calculations formally scales between $O(N^3)$ and $O(N^4)$, where N is proportional to the number of electrons, while MP2 formally scales as $O(N^5)$.[45]

2.4.3 Basis set effect on $\Delta E_{\mathrm{stored}}$

To ensure the basis set of single-point energy calculations is large enough, $\Delta E_{\mathrm{stored}}$ for the charging reaction of benzohydroquinone and anthraquinone to give benzoquinone and anthrahydroquinone was calculated using MP2 and B3LYP with various double- and triple-zeta Pople basis sets from 3-21G to 6-311+G(3df,p).[37,42,44] The results are given in Table 2.1.

Table 2.1: Calculated ΔE_{stored} (kJ mol^{-1}) for BH_2Q and AQ reacting to form BQ and AH_2Q at different basis sets using MP2 and B3LYP. Geometry optimisations for these calculations were performed at B3LYP/6-311G(2d,p).

Basis set	MP2	B3LYP
3-21G	-177.57	-146.94
6-311G	-157.90	-129.74
6-311G(d)	-157.04	-127.90
6-311+G	-149.99	-127.81
6-311G(d,p)	-156.26	-128.09
6-311G(2d,p)	-149.76	-123.75
6-311+G(2d,p)	-143.64	-106.45
6-311G(2d,2p)	-149.09	-117.54
6-311+G(3df,p)	-142.92	-113.14

The calculated values of ΔE_{stored} change as the size of the basis set increases up to convergence at 6-311+G(2d,p) for both MP2 and B3LYP. After this point adding more polarisation functions does not significantly change the value of ΔE_{stored} . The diffuse function is important, as the difference between results for basis sets identical except for a diffuse function is significant. The electron-rich oxygen atoms require the diffuse function to correctly account for the higher electron density. For single-point energy calculations in this work, the basis set 6-311+G(2d,p) will be used.

2.4.4 Zero-point energy and entropy corrections ($\Delta H_{\text{vibrational}}$)

The electrochemical potential of a redox reaction is negatively proportional to the change in Gibbs energy (ΔG) for the reaction. As shown in Equation 2.2, vibrational enthalpic and solute entropic effects are required for a comprehensive determination of ΔG. The ZPE is the largest component of these. However, the vibrational enthalpies and gas-phase entropies of the products and reactants (solutes) generally do not have a large effect on computed redox free energies, particularly for organic redox reactions.[46,47] Gas-phase Gibbs energies and enthalpies for the unsubstituted charging reaction were obtained by performing frequency analyses at B3LYP/6-311+G(2d,p) are given in Table 2.2.

Given that $\Delta G = -zFE^\circ$ where z is the number of electrons transferred, F is the Faraday constant and E° is the cell potential, the ΔG value of 119.8 kJ mol^{-1} is equivalent to a cell potential of -0.62 V and the ΔH value of 122.3 kJ mol^{-1} is equivalent to a cell potential of -0.63 V. Experimental two-electron reduction potentials for BQ and AQ are 0.643 V and 0.089 V respectively (vs NHE, in

Table 2.2: Gas-phase Gibbs energy and enthalpy changes for the charging reaction between anthraquinone and benzohydroquinone, calculated at B3LYP/6-311+G(2d,p) for 298 K.

Reaction coordinate	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	Difference (kJ mol^{-1})
$A + BH_2$	0	0	0
$A^{\bullet-} + BH_2^{\bullet+}$	589.5	592.88	3.31 (0.6%)
$AH^{\bullet} + BH^{\bullet}$	154.8	164.8	9.9 (6.5%)
$AH^{-} + BH^{+}$	729.8	735.4	5.6 (0.8%)
$AH_2 + B$	119.8	122.3	2.5 (2.1%)

aqueous acidic solution),[48] giving a cell potential of -0.554 V. While neither calculated cell potential aligns closely with the experimental value, the difference between the two calculated values is small.

The difference between calculated ΔH and ΔG is most significant for the second reaction stage, where two radical neutrals are present; it has a relative error of 6.5%. The relative error for ΔE_{stored} is 2.1%. The other interesting values are the errors in *differences* for the electron transfer steps – ΔE_1 and ΔE_2 – and there is a large degree of cancellation of errors for these (Table 2.3).

Table 2.3: Gas-phase Gibbs energy and enthalpy changes for the charging reaction between anthraquinone and benzohydroquinone, calculated at B3LYP/6-311+G(2d,p) for 298 K.

Reaction step	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	Absolute difference (kJ mol^{-1})
1 (e^- transfer)	589.57	592.88	3.31 (0.6%)
2 (H^+ transfer)	-434.73	-428.05	6.68 (1.5%)
3 (e^- transfer)	574.97	570.62	4.35 (0.8%)
4 (H^+ transfer)	-609.99	-613.11	3.12 (0.5%)

The relative error for the two electron transfer steps, ΔE_1 and ΔE_2, are 0.6% and 0.8%, respectively. Frequency calculations are very computationally expensive due to the intensive nature of finding second-order derivatives of energy with respect to nuclear displacement. However, they yield a small increase in accuracy. Therefore, changes in vibrational energy and gas-phase entropy are assumed to be negligible in this work. Equation 2.2 can therefore be simplified to Equation 2.3:

$$\Delta G \approx \Delta H_{\text{electronic}} + \Delta H_{\text{solvation}} - T\Delta S_{\text{solvation}} \tag{2.3}$$

2.4.5 Solvation modelling($\Delta H_{\text{solvation}}$, $\Delta S_{\text{solvation}}$)

Solvation has a stabilising effect on chemical species; a species in solution will be of lower energy than in the gas phase. The calculated reaction coordinates for the charging reaction between anthraquinone and benzohydroquinone in both the gas phase and in solution, modelled by C-PCM[39–41] with dielectric constants of 5, 10, 20 and 40, are shown in Figure 2.6.

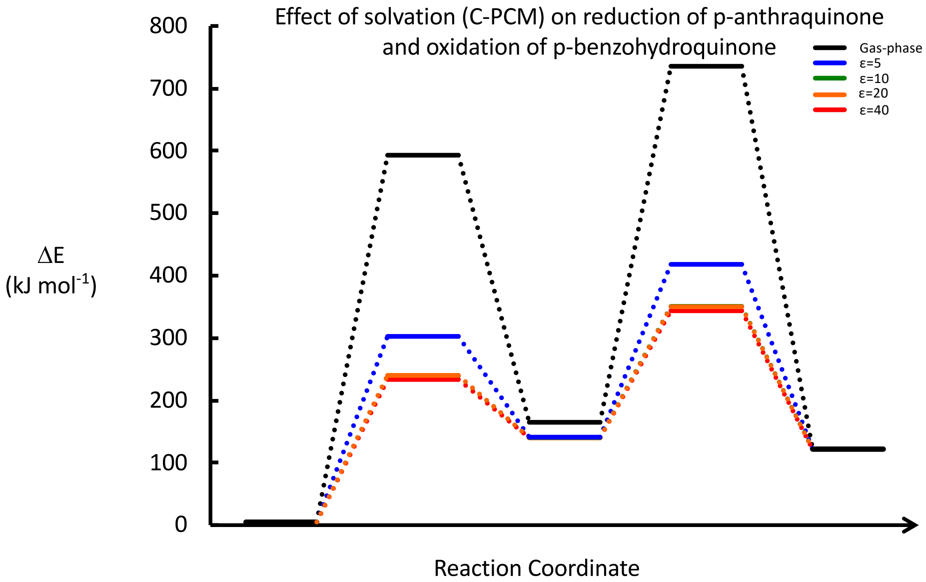


Figure 2.6: Calculated gas-phase and solvated reaction energy profiles for the oxidation of *p*-benzohydroquinone and reduction of *p*-anthraquinone. Solvation was modelled using C-PCM with dielectric constants of 5, 10, 20 and 40.

The steps involving ionic species are significantly stabilised due to the strong charge-dipole interaction. The step involving the two radical neutral species AHQ and BHQ is modestly stabilised, as the permanent dipole in the asymmetric species interacts with the solvent to a weaker extent. The products and reactants are not significantly stabilised by solvation because they lack permanent dipole moments. The magnitude of solvation stabilisation increases with dielectric to a limit. The change in energy from the gas-phase to a dielectric constant (ε) of 2 is larger than the change from $\varepsilon = 2$ to $\varepsilon = 5$. Increasing the dielectric constant past 5 does not significantly change the energy of solvation for the ionic species, and for the neutral species there is almost no change in solvation energy. A dielectric constant (ε) of 10 was chosen as it models a slightly polar solvent which dissolves quinones of different sizes and substitution patterns. Compare with the dielectric constants of benzene ($\varepsilon = 2$)[49] acetonitrile ($\varepsilon = 36$) and water ($\varepsilon = 78$).[50] The error due to solvation modelling approximations made by C-PCM is negligible for calculated values of ΔE_{stored} and is about 2.0% and 2.5% for calculated values of ΔE_1 and ΔE_2, respectively. Since Q-Chem reports C-PCM solvation effects as free energy values rather than separate enthalpic and entropic effects, the final description for the approximation of free energy changes is given by Equation 2.4:

$$\Delta G \approx \Delta H_{\text{electronic}} + \Delta G_{\text{solvation}} \tag{2.4}$$

2.5 Conclusions

A method has been benchmarked to reliably and efficiently determine the reaction coordinate diagrams and values of ΔE_1, ΔE_2 and ΔE_{stored} for the redox reaction between anthraquinone and benzohydroquinone to produce anthrahydroquinone and benzoquinone. It comprises a gas-phase geometry optimisation at B3LYP/6-311G(d) followed by a single-point energy calculation at B3LYP/6-311+G(2d,p). Solvation is modelled using C-PCM with a dielectric constant of 10. ZPE and gas-phase entropy are not required to achieve reliable results. The use of DFT rather than higher-level methods gives an uncertainty of 10% for calculated energy barrier heights, and 2% for energies stored. Ignoring entropic and vibrational enthalpic effects gives an uncertainty of 1% for barrier heights and 2% for energies stored. While solvation modelling error is approximately 3% for energy barriers only. This gives a total error of 14% for calculated barrier heights, and 4% for calculated values of ΔE_{stored}. When comparing like values, such as one values of ΔE_{stored} to another, there is a large degree of error cancellation, so these errors are reduced. This means that values of ΔE_{stored} are qualitatively quite reliable. This method will be used to study a range of quinones of different sizes and substitution patterns to identify quinones which are promising in building a photorechargeable battery by optimising the heights of the energy barriers and the amounts of energy stored.

Chapter 3

Functionalised quinones

3.1 Introduction

This chapter seeks to design substituted quinones for use in photorechargeable RFBs. The two aims are to maximise the amount of energy stored, $\Delta E_{\mathrm{stored}}$, and to optimise the reaction barrier heights, ΔE_1 and ΔE_2, so that they match the energy available from incident solar radiation. These quantities are shown on a reaction coordinate diagram in Figure 3.1. The chemical species present at each step along the reaction coordinate are illustrated in Figure 3.2.

The two aims are competing against each other to an extent, as increasing the value of $\Delta E_{\mathrm{stored}}$ will generally also increase the values of ΔE_1 and ΔE_2. The first step is an electron transfer from the benzohydroquinone to the anthraquinone to give two radical ions, which is an endothermic process. Proton transfer occurs to balance charges, giving two radical neutral semiquinone species. This is a spontaneous exothermic step. Another endothermic electron transfer takes place to give singlet ions, followed by a proton transfer to give benzoquinone and anthrahydroquinone that are less stable than the starting materials so energy is stored overall. To be photorechargeable, the energy required for the two endothermic electron-transfer steps must be provided by solar radiation.

First, the solar radiation is absorbed by a photovoltaic material. After an electron is promoted by a photon from the PV material's HOMO or valence band to its LUMO or conduction band, it is transferred from the PV material to the anthraquinone (Figure 3.3). An electron from the HOMO of the benzohydroquinone is transferred to the LUMO or valence band of the PV material to restore electrical neutrality in the PV material. The net effect is one electron is transferred from the HOMO

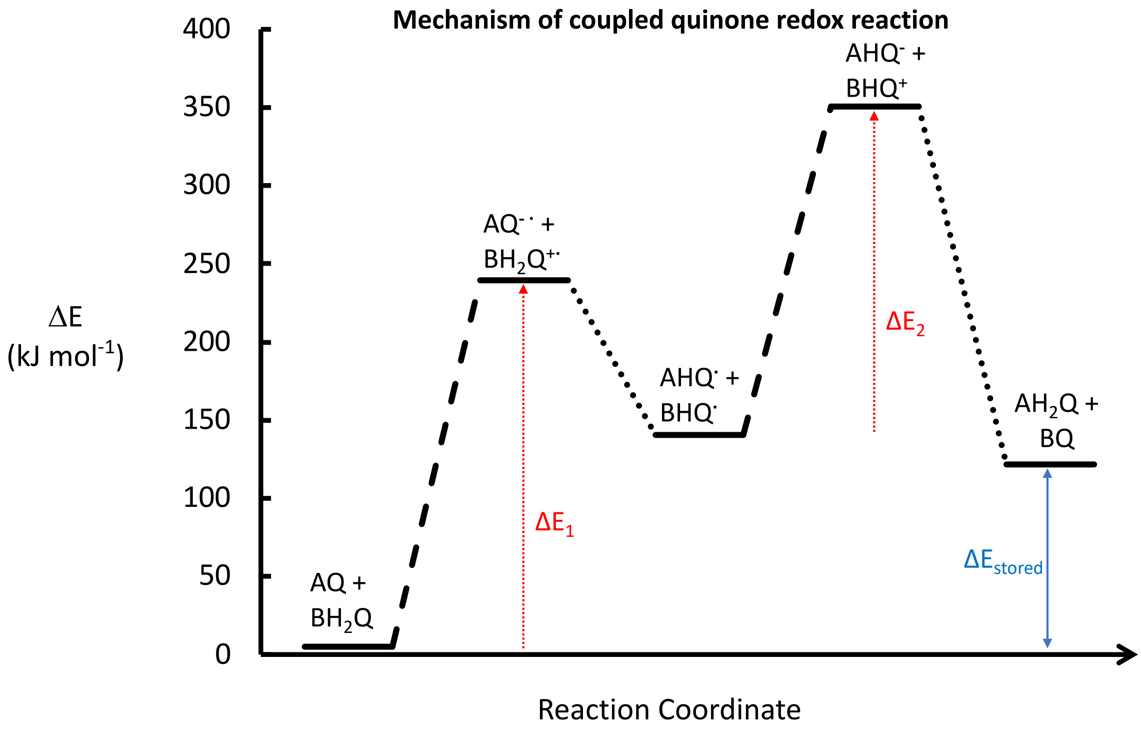


Figure 3.1: Reaction energy profile for the reduction of p-anthraquinone (AQ) and oxidation of p-benzohydroquinone (BH_2Q). Dashed lines represent electron transfer steps and dotted lines represent proton exchange steps. To create a photorechargeable battery, the energy barriers (ΔE_1 and ΔE_2) should be lowered, and the total energy stored (ΔE_{stored}) should be maximised.

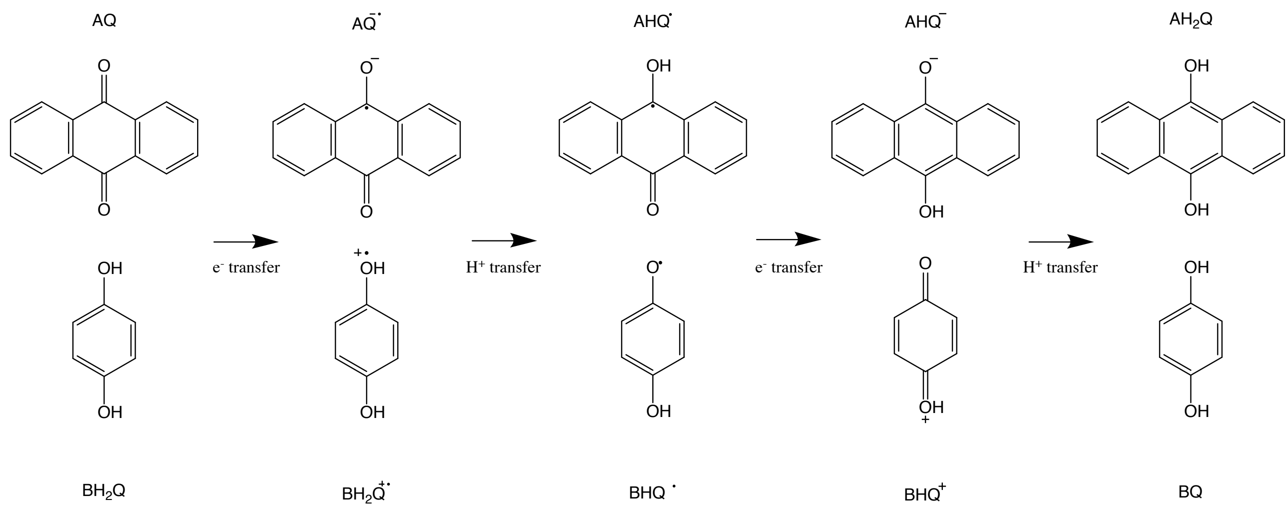


Figure 3.2: Reaction scheme for the reduction of anthraquinone and oxidation of benzohydroquinone. Reduced species are denoted AH_2Q and BH_2Q for anthrahydroquinone and benzohydroquinone, respectively

of the benzohydroquinone to the LUMO of the anthraquinone to give the benzohydroquinone radical cation ($BH_2Q^{\bullet+}$) and the anthrahydroquinone radical anion ($A^{\bullet-}$).

A proton is then transferred from the benzohydroquinone radical cation ($BH_2Q^{\bullet+}$) to the anthrahydroquinone radical anion ($A^{\bullet-}$), which slightly raises the energy of the benzosemiquinone orbitals and lowers the energy of the anthrasemiquinone orbitals and gives two radical semiquinone neutral species ($BH^{\bullet}$ and $AH^{\bullet}$). The process is repeated: a second electron transfer occurs, facilitated by pho-

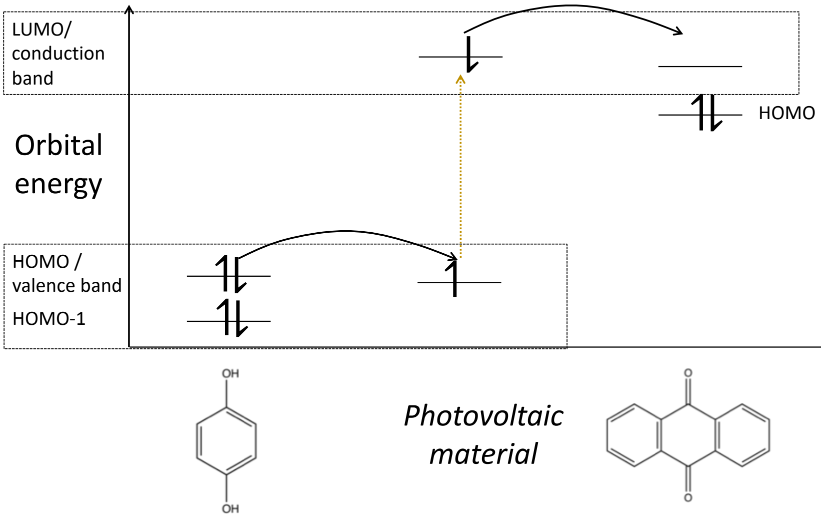


Figure 3.3: After the first photoexcitation, an electron is transferred from the HOMO of the benzohydroquinone via the photovoltaic material to the LUMO of the anthrahydroquinone. The brown dashed arrow indicates where photoexcitation has occurred and the black arrows indicate electron transfer.

toexcitation of a HOMO or valence-band electron in the PV material. This electron transfer gives a singlet benzoquinone cation (BHQ^+) and a singlet anthrahydroquinone anion (AHQ^-). Proton transfer gives benzoquinone (BQ) and anthrahydroquinone (AH_2Q) as products.

Overcoming the energy barriers of the endothermic electron-transfer steps with solar energy requires that they have an energy similar that of photons that are appreciably present in solar radiation. The values of ΔE_1 and ΔE_2 (Figure 3.1) should therefore lie within the approximate range of 0.8–2.0 eV (80–190 kJ mol^{-1}) to have Shockley-Quiesser efficiency limits of greater than 25% as the energy storage components of a photorechargeable battery.[30,31] A lead-acid battery, with two electrons transferred and a cell voltage of 2.1 V, stores 4.2 eV of energy,[51] while a lithium-ion battery has one electron-transfer and a voltage of 2.6 V, so stores 2.6 eV.[45] Therefore, the value of ΔE_{stored} should be increased from the reference value of the BQ/AH_2Q reaction of 1.26 eV to become more competitive with lead-acid and lithium-ion batteries.

In order to achieve these two goals, chemical modifications to the quinone scaffold will be made and tested computationally. Specifically, the size of the quinone ring system will be altered and molecules will be substituted with electron-donating and electron-withdrawing functional groups in a range of different substitution patterns.

3.2 Methods

3.2.1 Quantum chemical calculations

The reduction and oxidation reaction pathways for anthraquinones (A), naphthoquinones (N) and benzoquinones (B) and their respective reduced forms, anthrahydroquinones (AH_2), naphthohydroquinones (NH_2) and benzohydroquinones (BH_2) were calculated. All quinones investigated were *para*-isomers (1,4-benzoquinone, 1,4-naphthoquinone and 9,10-anthraquinone). Given their planar geometries, quinones cannot be fully substituted with non-linear groups. Therefore, only the singly-substituted and half-substituted quinones illustrated in Figure 3.4 were studied.

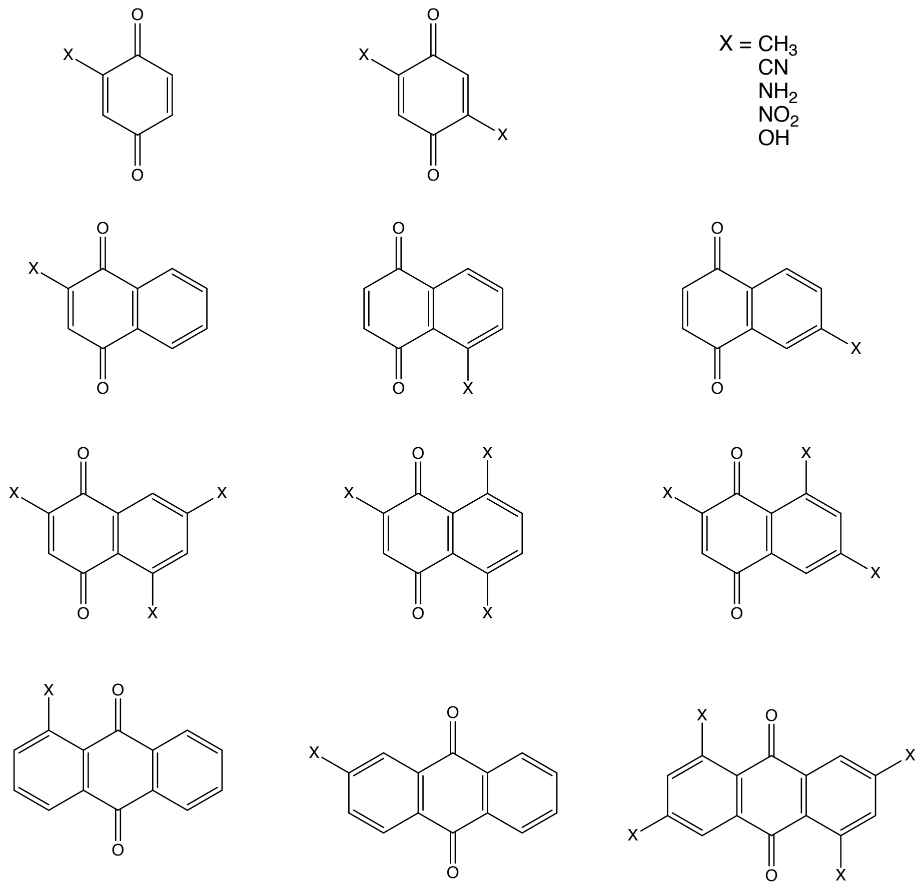


Figure 3.4: The substitution patterns of the quinones studied. X = CH_3, CN, NH_2, NO_2 or OH.
Top row: singly- and doubly-substituted benzoquinones; 2-X benzoquinone (2-XBQ) and 2,5-X benzoquinone (2,5-XBQ)
Second row: singly-substituted naphthoquinones; 2-X, 5-X and 6-X naphthoquinones
Third row: triply-substituted naphtoquinones; 2,5,7-X, 2,5,8-X and 2,6,8-X naphthoquinones
Bottom row: singly- and quadruply-substituted anthraquinones; 1-X, and 2-X and 1,3,5,8-X anthraquinones.

Single-point energies were calculated for each of the five species involved in each half-reaction (reactant, radical ion, radical neutral, singlet ion and product). Geometries were optimised for the three neutral species. Single-point energies were calculated for ions at the previous oxidation state geometry, modelling vertical electron transfer. All calculations were performed using the Q-Chem 4 quantum chemistry program package.[34] Neutral species geometries were optimised at B3LYP[35,36]/6-311G(d).[37] Single-point energy calculations were performed at B3LYP/6-311+G(2d,p).[37,42,44,52] Solvation was modelled with C-PCM[39–41] and a dielectric constant of 10, to model a slightly polar environment in which all the molecules studied in all redox states are soluble.

3.2.2 Data processing

The change in absolute energy of the first electron gain or loss were determined for each half-reaction as the difference in energy between the radical ion and reactant. The energy change for each combination of a reduction and an oxidation from the 58 quinones studied were added together, which gives the first energy barrier, ΔE_1, for each theoretical electrochemical cell, where a thermochemical electrochemical cell barrier height is defined as the energy of transferring an electron from one species to another. This process was repeated for the second energy barrier (ΔE_2) and the energy stored ($\Delta E_{\mathrm{stored}}$). In total, this gives ΔE_1, ΔE_2 and $\Delta E_{\mathrm{stored}}$ for $58^2 = 3364$ theoretical cells. Excluding cells were identical quinones were used (which store zero energy) and half of the remaining cells (in one configuration each cell will store energy while in reverse, the cell will give off energy), there are $\frac{1}{2} \times 58 \times 57 = 1653$ cells which store energy (rather than spontaneously reacting to release energy), and have their thermodynamic parameters (ΔE_1, ΔE_2 and $\Delta E_{\mathrm{stored}}$) determined in this work.

The redox pairs that will form the most efficient photorechargeable batteries will have the highest photorecharging efficiency index, P, which is defined here as:

$$P = f_{\mathrm{SQ}} \times \Delta E_{\mathrm{stored}} \tag{3.1}$$

where f_{SQ} is the fractional Shockley-Queisser efficiency[30,31] of the least efficient charging step in the charging reaction, and $\Delta E_{\mathrm{stored}}$ is the energy stored by the charging reaction. This gives a measure for how much energy can be stored upon photorecharging, given the solar radiation present at Earth's surface.

3.3 Results and discussion

The effect of ring system size on the reaction pathways of quinone reduction are explored in the reaction energy profiles of the reduction of benzoquinone, naphthoquinone and anthraquinone when coupled to the oxidation of benzohydroquinone. A similar exercise is carried out for oxidation of hydroquinones, coupled to the reduction of benzoquinone. The effect that functional group substitution has on quinone redox pathways is investigated by similar means: varying the degree and nature of substitution of a benzoquinone which is reduced (or oxidised) while coupling to an unsubstituted benzohydroquinone (or benzoquinone) which is oxidised (or reduced). The combination of these two effects is looked at and the pairs of quinones which store the most energy, and those which are best for photorecharging, are identified. The complete dataset of values of energy barriers and energies stored for each pair of quinone couples can be found in Appendix A.

3.3.1 Effect of ring system size

The effect of ring system size in unsubstituted quinones on the redox reaction pathway and the values of ΔE_1, ΔE_2 and ΔE_{stored} is summarised in reaction coordinate diagrams of the reduction (Figure 3.5) and oxidation (Figure 3.6) of different quinones. These diagrams describe the reverse reactions to each other, so the absolute energy differences between products and reactants are identical. All energies along each reaction pathway are computed relative to the energy of the reactants.

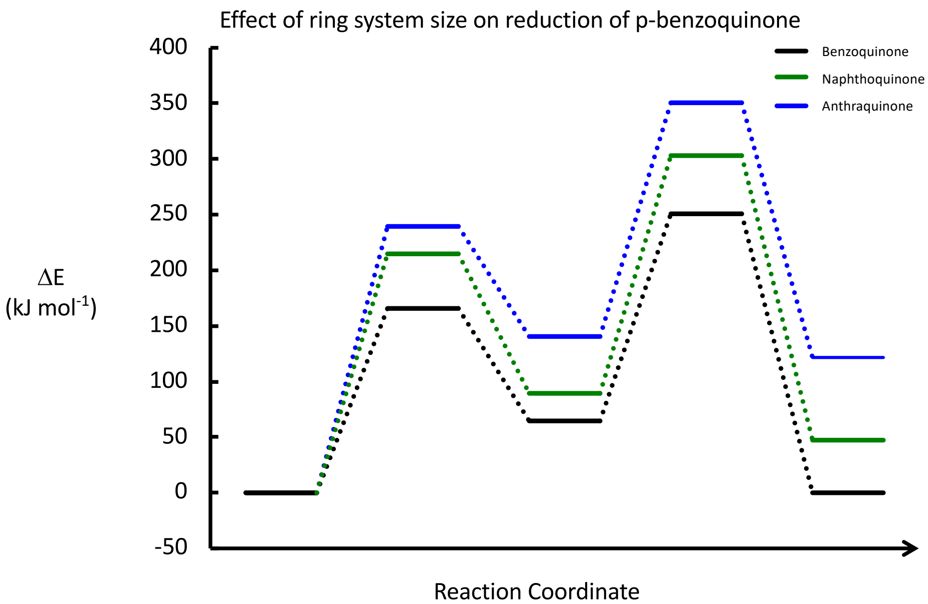


Figure 3.5: Reaction energy profile for the reduction of p-quinones of different sizes, coupled to oxidation of p-benzohydroquinone

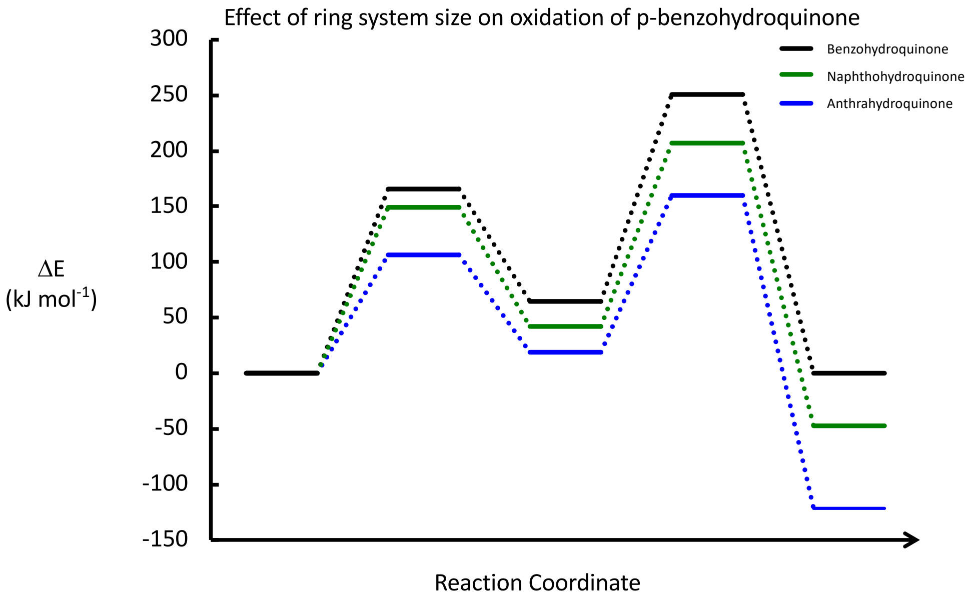


Figure 3.6: Reaction energy profile for the oxidation of *p*-hydroquinones of different sizes, coupled to reduction of *p*-benzoquinone

Extending the organic ring framework from benzoquinone to naphthoquinone to anthraquinone increases the energy required to reduce the quinone, but increases the amount of energy stored in the cell. The values of ΔE_1, ΔE_2 and ΔE_{stored} increase. Conversely, a more extended ring network decreases the amount of energy required to oxidise the hydroquinone, and stores less energy. Additional rings allow electrons to delocalise over more space, which lowers the energy of the molecular orbitals, and the values of ΔE_1, ΔE_2 and ΔE_{stored} decrease.

3.3.2 Effect of substitution

The effects of functional group substitution on the redox reaction pathway of *p*-benzoquinones is summarised in reaction coordinate diagrams of the reduction (Figure 3.7) and oxidation (Figure 3.8) of different quinones. These diagrams describe the reverse reaction to each other, so the absolute energy differences between products and reactants are identical.

The electron-donating groups -CH_3, -NH_2 and -OH lower the energy required for the oxidation process, and also lower the energy stored upon oxidation. Quinones substituted with electron donors are richer in electrons, so it is an easier process to remove electrons in oxidation (Figure 3.8), but a harder one to add electrons in reduction (Figure 3.7). Conversely, the electron-withdrawing groups -CN and -NO_2 increase the energies of oxidation and lower the energies of reduction.

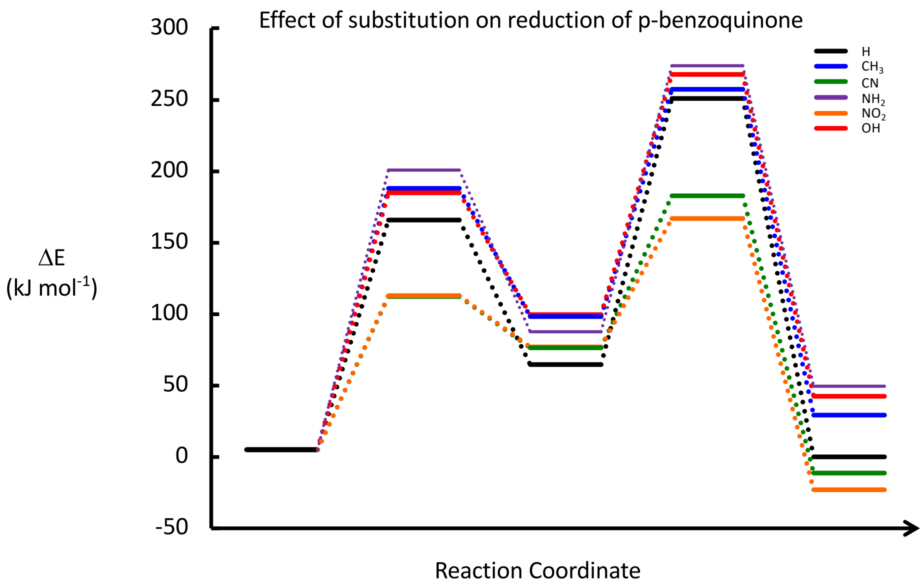


Figure 3.7: Reaction energy profile for the reduction of monosubstituted *p*-benzoquinones, coupled to oxidation of *p*-benzohydroquinone

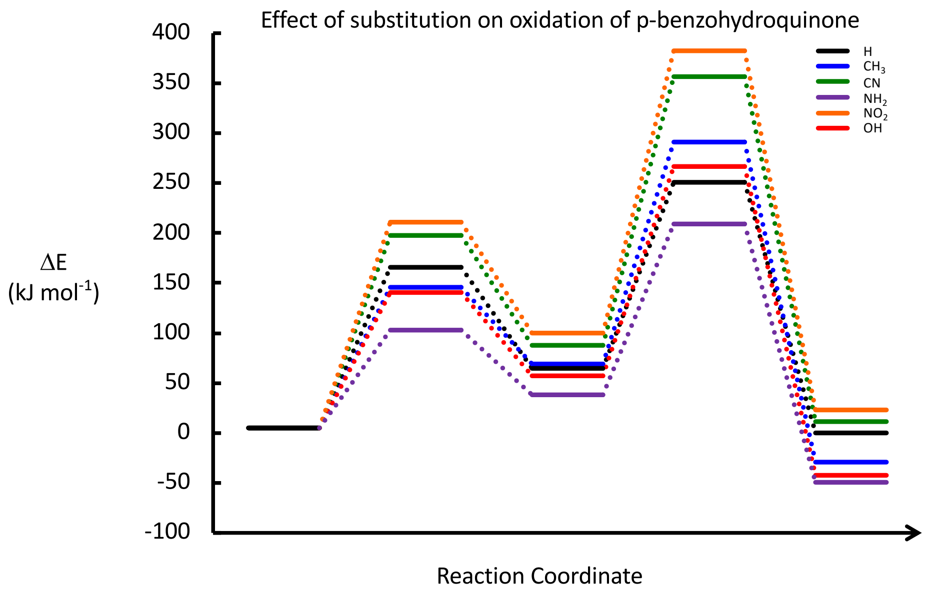


Figure 3.8: Reaction energy profile for the oxidation of monosubstituted *p*-benzohydroquinones, coupled to reduction of *p*-benzoquinone

3.3.3 Combined effect of ring system size and substitution on energy stored

Combining the two effects of ring system size and substitution requires inspection of every combination of quinone and benzoquinone pair. Tables 3.2 to 3.8 give the $\Delta E_{\mathrm{stored}}$ values for each possible cell. The tables are laid out with quinones becoming more substituted left-to-right and top-to-bottom. In each block of five (dashed lines), the substituents are ordered from most electron-donating (NH_2) to most electron-withdrawing (NO_2). It is clear that the values of $\Delta E_{\mathrm{stored}}$ increase in these blocks left-to-right, as the oxidised species become more electron-poor, and decrease from top-to-bottom, as the reduced species becomes more electron-rich.

There are two criteria by which the best combinations of quinone couples can be selected: maximising the amount of energy stored and optimising the charging barrier heights so that they make the most efficient use of the solar radiation at Earth's surface. Those pairs of couples which store the most energy are given below (Table 3.1).

Reduced upon charging	Oxidised upon charging	ΔE_{stored} (eV)	ΔE_{stored} (kJ mol^{-1})
1,3,5,7-NH_2AQ	2,5-NO_2BH_2Q	2.68	259
1,3,5,7-NH_2AQ	2,6,8-NO_2NH_2Q	2.48	239
1,3,5,7-NH_2AQ	2,5-$CNBH_2Q$	2.46	237
1,3,5,7-NH_2AQ	2-NO_2BH_2Q	2.41	232
1,3,5,7-NH_2AQ	2,5,8-NO_2NH_2Q	2.41	232
1-NH_2AQ	2,5-NO_2BH_2Q	2.36	228

Table 3.1: Pairs of quinone which store the most energy upon charging

All of the highest-storage combinations comprise an anthraquinone with amino groups and a benzohydroquinone or naphthohydroquinone with nitro or cyano groups. For example, the redox couple that stores the most energy is illustrated in Figure 3.9. In each case this gives an electron-rich electron acceptor and an electron-poor electron donor. Since these reagents are the most difficult to reduce and oxidise, respectively, much energy is required to do so. Electrons are moved from an electron-poor molecule to an electron-rich molecule and a high amount of energy is stored.

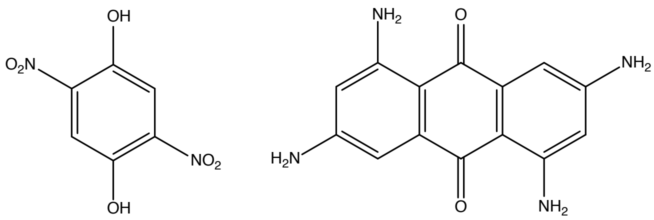


Figure 3.9: 2,5-NO_2BH_2Q and 1,3,5,7-NH_2AQ, the two quinones which store the most energy (2.68 eV) when simultaneously oxidised and reduced, respectively

For each combination of quinone and hydroquinone the ΔE_{stored} was determined. 1,653 electrochemical cells were studied and the distribution of values of ΔE_{stored} is given in Table 3.2.

ΔE_{stored} (eV)	Number of redox pairs
0–0.5	648
0.5–1.0	549
1.0–1.5	282
1.5–2.0	143
2.0–2.5	30
2.5–3.0	1

Table 3.2: Ranges of ΔE_{stored} and how many of the potential substituted redox pairs lie in each range

Table 3.3: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of benzohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised BH_2Q	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	2,5-NH_2	2,5-OH	2,5-CH_3	2,5-CN	2,5-NO_2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.2437	1.2248	1.2275	1.2325	1.248	1.2524	1.195	1.2142	1.2273	1.2543	1.2625
Benzoquinones												
H	-1.2437	0	-0.5122	-0.4395	-0.3028	0.1175	0.2384	-1.3228	-0.8011	-0.4454	0.289	0.5118
2-NH_2	-1.2248	0.5122	0	0.0728	0.2094	0.6297	0.7506	-0.8106	-0.2889	0.0669	0.8013	1.024
2-OH	-1.2275	0.4395	-0.0728	0	0.1367	0.5569	0.6779	-0.8833	-0.3616	-0.0059	0.7285	0.9512
2-CH_3	-1.2325	0.3028	-0.2094	-0.1367	0	0.4203	0.5412	-1.02	-0.4983	-0.1425	0.5918	0.8146
2-CN	-1.248	-0.1175	-0.6297	-0.5569	-0.4203	0	0.1209	-1.4403	-0.9186	-0.5628	0.1716	0.3943
2-NO_2	-1.2524	-0.2384	-0.7506	-0.6779	-0.5412	-0.1209	0	-1.5612	-1.0395	-0.6837	0.0506	0.2734
2,5-NH_2	-1.195	1.3228	0.8106	0.8833	1.02	1.4403	1.5612	0	0.5217	0.8775	1.6118	1.8346
2,5-OH	-1.2142	0.8011	0.2889	0.3616	0.4983	0.9186	1.0395	-0.5217	0	0.3557	1.0901	1.3128
2,5-CH_3	-1.2273	0.4454	-0.0669	0.0059	0.1425	0.5628	0.6837	-0.8775	-0.3557	0	0.7344	0.9571
2,5-CN	-1.2543	-0.289	-0.8013	-0.7285	-0.5918	-0.1716	-0.0506	-1.6118	-1.0901	-0.7344	0	0.2227
2,5-NO_2	-1.2625	-0.5118	-1.024	-0.9512	-0.8146	-0.3943	-0.2734	-1.8346	-1.3128	-0.9571	-0.2227	0
Naphthoquinones												
H	-1.2256	0.4904	-0.0219	0.0509	0.1876	0.6078	0.7288	-0.8324	-0.3107	0.045	0.7794	1.0021
2-NH_2	-1.1993	1.2076	0.6954	0.7682	0.9048	1.3251	1.446	-0.1152	0.4065	0.7623	1.4967	1.7194
2-OH	-1.2067	1.0053	0.493	0.5658	0.7025	1.1227	1.2437	-0.3175	0.2042	0.5599	1.2943	1.517
2-CH_3	-1.2105	0.9013	0.3891	0.4619	0.5985	1.0188	1.1397	-0.4215	0.1002	0.456	1.1904	1.4131
2-CN	-1.2476	-0.1063	-0.6186	-0.5458	-0.4092	0.0111	0.132	-1.4292	-0.9074	-0.5517	0.1827	0.4054
2-NO_2	-1.2295	0.3861	-0.1262	-0.0534	0.0833	0.5036	0.6245	-0.9367	-0.415	-0.0593	0.6751	0.8978
5-NH_2	-1.2082	0.9658	0.4536	0.5264	0.663	1.0833	1.2042	-0.357	0.1648	0.5205	1.2549	1.4776
5-OH	-1.2121	0.8583	0.3461	0.4188	0.5555	0.9758	1.0967	-0.4645	0.0572	0.4129	1.1473	1.37
5-CH_3	-1.2123	0.8523	0.34	0.4128	0.5495	0.9698	1.0907	-0.4705	0.0512	0.4069	1.1413	1.364
5-CN	-1.2191	0.668	0.1557	0.2285	0.3652	0.7855	0.9064	-0.6548	-0.1331	0.2226	0.957	1.1797
5-NO_2	-1.2238	0.539	0.0267	0.0995	0.2362	0.6565	0.7774	-0.7838	-0.2621	0.0936	0.828	1.0507
6-NH_2	-1.2103	0.9073	0.395	0.4678	0.6045	1.0248	1.1457	-0.4155	0.1062	0.4619	1.1963	1.419
6-OH	-1.2134	0.8225	0.3102	0.383	0.5197	0.9399	1.0609	-0.5003	0.0214	0.3771	1.1115	1.3342
6-CH_3	-1.2138	0.8133	0.3011	0.3738	0.5105	0.9308	1.0517	-0.5095	0.0122	0.3679	1.1023	1.3251
6-CN	-1.2215	0.603	0.0908	0.1635	0.3002	0.7205	0.8414	-0.7198	-0.1981	0.1576	0.892	1.1147
6-NO_2	-1.2244	0.5235	0.0113	0.0841	0.2207	0.641	0.7619	-0.7993	-0.2776	0.0782	0.8126	1.0353
2,5,7-NH_2	-1.191	1.4329	0.9207	0.9935	1.1301	1.5504	1.6713	0.1101	0.6319	0.9876	1.722	1.9447
2,5,7-OH	-1.2115	0.8746	0.3624	0.4352	0.5718	0.9921	1.113	-0.4482	0.0736	0.4293	1.1637	1.3864
2,5,7-CH_3	-1.2159	0.7557	0.2435	0.3162	0.4529	0.8732	0.9941	-0.5671	-0.0454	0.3104	1.0447	1.2675
2,5,7-CN	-1.2423	0.0375	-0.4748	-0.402	-0.2653	0.155	0.2759	-1.2853	-0.7636	-0.4079	0.3265	0.5492
2,5,7-NO_2	-1.2425	0.0325	-0.4798	-0.407	-0.2703	0.1499	0.2708	-1.2903	-0.7686	-0.4129	0.3215	0.5442
2,5,8-NH_2	-1.1832	1.6464	1.1341	1.2069	1.3436	1.7638	1.8848	0.3236	0.8453	1.201	1.9354	2.1581
2,5,8-OH	-1.207	0.9976	0.4854	0.5581	0.6948	1.1151	1.236	-0.3252	0.1965	0.5523	1.2866	1.5094
2,5,8-CH_3	-1.2133	0.8247	0.3125	0.3852	0.5219	0.9422	1.0631	-0.4981	0.0236	0.3793	1.1137	1.3365
2,5,8-CN	-1.2397	0.1076	-0.4046	-0.3319	-0.1952	0.2251	0.346	-1.2152	-0.6935	-0.3378	0.3966	0.6194
2,5,8-NO_2	-1.2523	-0.2351	-0.7473	-0.6745	-0.5379	-0.1176	0.0033	-1.5579	-1.0361	-0.6804	0.054	0.2767
2,6,8-NH_2	-1.1796	1.7417	1.2295	1.3023	1.4389	1.8592	1.9801	0.4189	0.9406	1.2964	2.0308	2.2535
2,6,8-OH	-1.206	1.0257	0.5135	0.5862	0.7229	1.1432	1.2641	-0.2971	0.2246	0.5804	1.3147	1.5375
2,6,8-CH_3	-1.2152	0.7748	0.2626	0.3354	0.472	0.8923	1.0132	-0.548	-0.0262	0.3295	1.0639	1.2866
2,6,8-CN	-1.242	0.0463	-0.4659	-0.3931	-0.2565	0.1638	0.2847	-1.2765	-0.7547	-0.399	0.3354	0.5581
2,6,8-NO_2	-1.2551	-0.3108	-0.823	-0.7503	-0.6136	-0.1933	-0.0724	-1.6336	-1.1119	-0.7562	-0.0218	0.201
Anthraquinones												
H	-1.1973	1.2604	0.7482	0.821	0.9576	1.3779	1.4988	-0.0624	0.4593	0.8151	1.5495	1.7722
1-NH_2	-1.1756	1.853	1.3408	1.4135	1.5502	1.9705	2.0914	0.5302	1.0519	1.4076	2.142	2.3648
1-OH	-1.1796	1.7436	1.2314	1.3042	1.4408	1.8611	1.982	0.4208	0.9425	1.2983	2.0327	2.2554
1-CH_3	-1.2184	0.6866	0.1744	0.2472	0.3838	0.8041	0.925	-0.6362	-0.1144	0.2413	0.9757	1.1984
1-CN	-1.1908	1.4371	0.9249	0.9977	1.1343	1.5546	1.6755	0.1143	0.6361	0.9918	1.7262	1.9489
1-NO_2	-1.1927	1.3867	0.8744	0.9472	1.0839	1.5042	1.6251	0.0639	0.5856	0.9413	1.6757	1.8984
2-NH_2	-1.1794	1.748	1.2358	1.3086	1.4452	1.8655	1.9864	0.4252	0.9469	1.3027	2.0371	2.2598
2-OH	-1.1824	1.6676	1.1554	1.2281	1.3648	1.7851	1.906	0.3448	0.8665	1.2223	1.9566	2.1794
2-CH_3	-1.1827	1.6596	1.1474	1.2202	1.3568	1.7771	1.898	0.3368	0.8585	1.2143	1.9487	2.1714
2-CN	-1.1915	1.4197	0.9074	0.9802	1.1169	1.5371	1.6581	0.0969	0.6186	0.9743	1.7087	1.9314
2-NO_2	-1.1939	1.3528	0.8405	0.9133	1.05	1.4702	1.5912	0.03	0.5517	0.9074	1.6418	1.8645
1,3,5,7-NH_2	-1.1639	2.1702	1.6579	1.7307	1.8674	2.2876	2.4085	0.8474	1.3691	1.7248	2.4592	2.6819
1,3,5,7-OH	-1.1862	1.5647	1.0525	1.1252	1.2619	1.6822	1.8031	0.2419	0.7636	1.1194	1.8537	2.0765
1,3,5,7-CH_3	-1.1871	1.5395	1.0273	1.1	1.2367	1.657	1.7779	0.2167	0.7384	1.0941	1.8285	2.0512
1,3,5,7-CN	-1.2129	0.8359	0.3237	0.3964	0.5331	0.9534	1.0743	-0.4869	0.0348	0.3905	1.1249	1.3476
1,3,5,7-NO_2	-1.2216	0.6008	0.0886	0.1613	0.298	0.7183	0.8392	-0.722	-0.2003	0.1555	0.8898	1.1126

Table 3.4: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	H	2-NH2	2-OH	2-CH3	2-CN	2-NO2	5-NH2	5-OH	5-CH3	5-CN	5-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.2256	1.1993	1.2067	1.2105	1.2476	1.2295	1.2082	1.2121	1.2123	1.2191	1.2238
Benzoquinones												
H	-1.2437	-0.4904	-1.2076	-1.0053	-0.9013	0.1063	-0.3861	-0.9658	-0.8583	-0.8523	-0.668	-0.539
2-NH2	-1.2248	0.0219	-0.6954	-0.493	-0.3891	0.6186	0.1262	-0.4536	-0.3461	-0.34	-0.1557	-0.0267
2-OH	-1.2275	-0.0509	-0.7682	-0.5658	-0.4619	0.5458	0.0534	-0.5264	-0.4188	-0.4128	-0.2285	-0.0995
2-CH3	-1.2325	-0.1876	-0.9048	-0.7025	-0.5985	0.4092	-0.0833	-0.663	-0.5555	-0.5495	-0.3652	-0.2362
2-CN	-1.248	-0.6078	-1.3251	-1.1227	-1.0188	-0.0111	-0.5036	-1.0833	-0.9758	-0.9698	-0.7855	-0.6565
2-NO2	-1.2524	-0.7288	-1.446	-1.2437	-1.1397	-0.132	-0.6245	-1.2042	-1.0967	-1.0907	-0.9064	-0.7774
2,5-NH2	-1.195	0.8324	0.1152	0.3175	0.4215	1.4292	0.9367	0.357	0.4645	0.4705	0.6548	0.7838
2,5-OH	-1.2142	0.3107	-0.4065	-0.2042	-0.1002	0.9074	0.415	-0.1648	-0.0572	-0.0512	0.1331	0.2621
2,5-CH3	-1.2273	-0.045	-0.7623	-0.5599	-0.456	0.5517	0.0593	-0.5205	-0.4129	-0.4069	-0.2226	-0.0936
2,5-CN	-1.2543	-0.7794	-1.4967	-1.2943	-1.1904	-0.1827	-0.6751	-1.2549	-1.1473	-1.1413	-0.957	-0.828
2,5-NO2	-1.2625	-1.0021	-1.7194	-1.517	-1.4131	-0.4054	-0.8978	-1.4776	-1.37	-1.364	-1.1797	-1.0507
Naphthoquinones												
H	-1.2256	0	-0.7173	-0.5149	-0.411	0.5967	0.1043	-0.4755	-0.3679	-0.3619	-0.1776	-0.0486
2-NH2	-1.1993	0.7173	0	0.2024	0.3063	1.314	0.8215	0.2418	0.3493	0.3553	0.5396	0.6687
2-OH	-1.2067	0.5149	-0.2024	0	0.1039	1.1116	0.6192	0.0394	0.147	0.153	0.3373	0.4663
2-CH3	-1.2105	0.411	-0.3063	-0.1039	0	1.0077	0.5152	-0.0645	0.043	0.049	0.2333	0.3624
2-CN	-1.2476	-0.5967	-1.314	-1.1116	-1.0077	0	-0.4924	-1.0722	-0.9646	-0.9586	-0.7743	-0.6453
2-NO2	-1.2295	-0.1043	-0.8215	-0.6192	-0.5152	0.4924	0	-0.5798	-0.4722	-0.4662	-0.2819	-0.1529
5-NH2	-1.2082	0.4755	-0.2418	-0.0394	0.0645	1.0722	0.5798	0	0.1076	0.1136	0.2979	0.4269
5-OH	-1.2121	0.3679	-0.3493	-0.147	-0.043	0.9646	0.4722	-0.1076	0	0.006	0.1903	0.3193
5-CH3	-1.2123	0.3619	-0.3553	-0.153	-0.049	0.9586	0.4662	-0.1136	-0.006	0	0.1843	0.3133
5-CN	-1.2191	0.1776	-0.5396	-0.3373	-0.2333	0.7743	0.2819	-0.2979	-0.1903	-0.1843	0	0.129
5-NO2	-1.2238	0.0486	-0.6687	-0.4663	-0.3624	0.6453	0.1529	-0.4269	-0.3193	-0.3133	-0.129	0
6-NH2	-1.2103	0.4169	-0.3004	-0.098	0.0059	1.0136	0.5212	-0.0586	0.049	0.055	0.2393	0.3683
6-OH	-1.2134	0.3321	-0.3852	-0.1828	-0.0789	0.9288	0.4364	-0.1434	-0.0358	-0.0298	0.1545	0.2835
6-CH3	-1.2138	0.3229	-0.3943	-0.192	-0.088	0.9196	0.4272	-0.1525	-0.045	-0.039	0.1453	0.2743
6-CN	-1.2215	0.1126	-0.6046	-0.4023	-0.2983	0.7093	0.2169	-0.3629	-0.2553	-0.2493	-0.065	0.064
6-NO2	-1.2244	0.0331	-0.6841	-0.4817	-0.3778	0.6299	0.1374	-0.4423	-0.3348	-0.3288	-0.1445	-0.0155
2,5,7-NH2	-1.191	0.9426	0.2253	0.4277	0.5316	1.5393	1.0469	0.4671	0.5747	0.5807	0.765	0.894
2,5,7-OH	-1.2115	0.3843	-0.333	-0.1306	-0.0267	0.981	0.4886	-0.0912	0.0164	0.0224	0.2067	0.3357
2,5,7-CH3	-1.2159	0.2653	-0.4519	-0.2496	-0.1456	0.8621	0.3696	-0.2101	-0.1026	-0.0966	0.0877	0.2167
2,5,7-CN	-1.2423	-0.4529	-1.1701	-0.9678	-0.8638	0.1438	-0.3486	-0.9284	-0.8208	-0.8148	-0.6305	-0.5015
2,5,7-NO2	-1.2425	-0.4579	-1.1752	-0.9728	-0.8689	0.1388	-0.3536	-0.9334	-0.8258	-0.8198	-0.6355	-0.5065
2,5,8-NH2	-1.1832	1.156	0.4387	0.6411	0.745	1.7527	1.2603	0.6805	0.7881	0.7941	0.9784	1.1074
2,5,8-OH	-1.207	0.5072	-0.21	-0.0077	0.0963	1.104	0.6115	0.0318	0.1393	0.1453	0.3296	0.4586
2,5,8-CH3	-1.2133	0.3343	-0.3829	-0.1806	-0.0766	0.931	0.4386	-0.1412	-0.0336	-0.0276	0.1567	0.2857
2,5,8-CN	-1.2397	-0.3828	-1.1	-0.8977	-0.7937	0.2139	-0.2785	-0.8582	-0.7507	-0.7447	-0.5604	-0.4314
2,5,8-NO2	-1.2523	-0.7254	-1.4427	-1.2403	-1.1364	-0.1287	-0.6211	-1.2009	-1.0933	-1.0873	-0.903	-0.774
2,6,8-NH2	-1.1796	1.2514	0.5341	0.7365	0.8404	1.8481	1.3556	0.7759	0.8834	0.8894	1.0737	1.2028
2,6,8-OH	-1.206	0.5353	-0.1819	0.0204	0.1244	1.1321	0.6396	0.0599	0.1674	0.1734	0.3577	0.4867
2,6,8-CH3	-1.2152	0.2845	-0.4328	-0.2304	-0.1265	0.8812	0.3888	-0.191	-0.0834	-0.0774	0.1069	0.2359
2,6,8-CN	-1.242	-0.444	-1.1613	-0.9589	-0.855	0.1527	-0.3397	-0.9195	-0.8119	-0.8059	-0.6216	-0.4926
2,6,8-NO2	-1.2551	-0.8012	-1.5184	-1.3161	-1.2121	-0.2045	-0.6969	-1.2767	-1.1691	-1.1631	-0.9788	-0.8498
Anthraquinones												
H	-1.1973	0.77	0.0528	0.2552	0.3591	1.3668	0.8743	0.2946	0.4021	0.4081	0.5924	0.7214
1-NH2	-1.1756	1.3626	0.6454	0.8477	0.9517	1.9593	1.4669	0.8871	0.9947	1.0007	1.185	1.314
1-OH	-1.1796	1.2533	0.536	0.7384	0.8423	1.85	1.3575	0.7778	0.8853	0.8913	1.0756	1.2046
1-CH3	-1.2184	0.1963	-0.521	-0.3186	-0.2147	0.793	0.3006	-0.2792	-0.1716	-0.1656	0.0187	0.1477
1-CN	-1.1908	0.9468	0.2295	0.4319	0.5358	1.5435	1.0511	0.4713	0.5789	0.5849	0.7692	0.8982
1-NO2	-1.1927	0.8963	0.1791	0.3814	0.4854	1.493	1.0006	0.4208	0.5284	0.5344	0.7187	0.8477
2-NH2	-1.1794	1.2577	0.5404	0.7428	0.8467	1.8544	1.3619	0.7822	0.8897	0.8958	1.0801	1.2091
2-OH	-1.1824	1.1772	0.46	0.6623	0.7663	1.774	1.2815	0.7018	0.8093	0.8153	0.9996	1.1286
2-CH3	-1.1827	1.1693	0.452	0.6544	0.7583	1.766	1.2735	0.6938	0.8013	0.8073	0.9916	1.1207
2-CN	-1.1915	0.9293	0.212	0.4144	0.5183	1.526	1.0336	0.4538	0.5614	0.5674	0.7517	0.8807
2-NO2	-1.1939	0.8624	0.1451	0.3475	0.4514	1.4591	0.9667	0.3869	0.4945	0.5005	0.6848	0.8138
1,3,5,7-NH2	-1.1639	1.6798	0.9625	1.1649	1.2688	2.2765	1.7841	1.2043	1.3119	1.3179	1.5022	1.6312
1,3,5,7-OH	-1.1862	1.0743	0.3571	0.5594	0.6634	1.6711	1.1786	0.5989	0.7064	0.7124	0.8967	1.0257
1,3,5,7-CH3	-1.1871	1.0491	0.3319	0.5342	0.6382	1.6458	1.1534	0.5736	0.6812	0.6872	0.8715	1.0005
1,3,5,7-CN	-1.2129	0.3455	-0.3717	-0.1694	-0.0654	0.9422	0.4498	-0.13	-0.0224	-0.0164	0.1679	0.2969
1,3,5,7-NO2	-1.2216	0.1104	-0.6068	-0.4045	-0.3005	0.7072	0.2147	-0.365	-0.2575	-0.2515	-0.0672	0.0618

Table 3.5: $\Delta E_{\mathrm{stored}}$ (eV) for coupled redox reactions involving oxidation of napthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	6-NH2	6-OH	6-CH3	6-CN	6-NO2	2,5,7-NH2	2,5,7-OH	2,5,7-CH3	2,5,7-CN	2,5,7-NO2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	1.2103	1.2134	1.2138	1.2215	1.2244	1.191	1.2115	1.2159	1.2423	1.2425
Benzoquinones											
H	-1.2437	-0.9073	-0.8225	-0.8133	-0.603	-0.5235	-1.4329	-0.8746	-0.7557	-0.0375	-0.0325
2-NH2	-1.2248	-0.395	-0.3102	-0.3011	-0.0908	-0.0113	-0.9207	-0.3624	-0.2435	0.4748	0.4798
2-OH	-1.2275	-0.4678	-0.383	-0.3738	-0.1635	-0.0841	-0.9935	-0.4352	-0.3162	0.402	0.407
2-CH3	-1.2325	-0.6045	-0.5197	-0.5105	-0.3002	-0.2207	-1.1301	-0.5718	-0.4529	0.2653	0.2703
2-CN	-1.248	-1.0248	-0.9399	-0.9308	-0.7205	-0.641	-1.5504	-0.9921	-0.8732	-0.155	-0.1499
2-NO2	-1.2524	-1.1457	-1.0609	-1.0517	-0.8414	-0.7619	-1.6713	-1.113	-0.9941	-0.2759	-0.2708
2,5-NH2	-1.195	0.4155	0.5003	0.5095	0.7198	0.7993	-0.1101	0.4482	0.5671	1.2853	1.2903
2,5-OH	-1.2142	-0.1062	-0.0214	-0.0122	0.1981	0.2776	-0.6319	-0.0736	0.0454	0.7636	0.7686
2,5-CH3	-1.2273	-0.4619	-0.3771	-0.3679	-0.1576	-0.0782	-0.9876	-0.4293	-0.3104	0.4079	0.4129
2,5-CN	-1.2543	-1.1963	-1.1115	-1.1023	-0.892	-0.8126	-1.722	-1.1637	-1.0447	-0.3265	-0.3215
2,5-NO2	-1.2625	-1.419	-1.3342	-1.3251	-1.1147	-1.0353	-1.9447	-1.3864	-1.2675	-0.5492	-0.5442
Naphthoquinones											
H	-1.2256	-0.4169	-0.3321	-0.3229	-0.1126	-0.0331	-0.9426	-0.3843	-0.2653	0.4529	0.4579
2-NH2	-1.1993	0.3004	0.3852	0.3943	0.6046	0.6841	-0.2253	0.333	0.4519	1.1701	1.1752
2-OH	-1.2067	0.098	0.1828	0.192	0.4023	0.4817	-0.4277	0.1306	0.2496	0.9678	0.9728
2-CH3	-1.2105	-0.0059	0.0789	0.088	0.2983	0.3778	-0.5316	0.0267	0.1456	0.8638	0.8689
2-CN	-1.2476	-1.0136	-0.9288	-0.9196	-0.7093	-0.6299	-1.5393	-0.981	-0.8621	-0.1438	-0.1388
2-NO2	-1.2295	-0.5212	-0.4364	-0.4272	-0.2169	-0.1374	-1.0469	-0.4886	-0.3696	0.3486	0.3536
5-NH2	-1.2082	0.0586	0.1434	0.1525	0.3629	0.4423	-0.4671	0.0912	0.2101	0.9284	0.9334
5-OH	-1.2121	-0.049	0.0358	0.045	0.2553	0.3348	-0.5747	-0.0164	0.1026	0.8208	0.8258
5-CH3	-1.2123	-0.055	0.0298	0.039	0.2493	0.3288	-0.5807	-0.0224	0.0966	0.8148	0.8198
5-CN	-1.2191	-0.2393	-0.1545	-0.1453	0.065	0.1445	-0.765	-0.2067	-0.0877	0.6305	0.6355
5-NO2	-1.2238	-0.3683	-0.2835	-0.2743	-0.064	0.0155	-0.894	-0.3357	-0.2167	0.5015	0.5065
6-NH2	-1.2103	0	0.0848	0.094	0.3043	0.3838	-0.5257	0.0326	0.1516	0.8698	0.8748
6-OH	-1.2134	-0.0848	0	0.0092	0.2195	0.2989	-0.6105	-0.0522	0.0668	0.785	0.79
6-CH3	-1.2138	-0.094	-0.0092	0	0.2103	0.2898	-0.6196	-0.0613	0.0576	0.7758	0.7808
6-CN	-1.2215	-0.3043	-0.2195	-0.2103	0	0.0795	-0.83	-0.2717	-0.1527	0.5655	0.5705
6-NO2	-1.2244	-0.3838	-0.2989	-0.2898	-0.0795	0	-0.9094	-0.3511	-0.2322	0.486	0.4911
2,5,7-NH2	-1.191	0.5257	0.6105	0.6196	0.83	0.9094	0	0.5583	0.6772	1.3955	1.4005
2,5,7-OH	-1.2115	-0.0326	0.0522	0.0613	0.2717	0.3511	-0.5583	0	0.1189	0.8372	0.8422
2,5,7-CH3	-1.2159	-0.1516	-0.0668	-0.0576	0.1527	0.2322	-0.6772	-0.1189	0	0.7182	0.7232
2,5,7-CN	-1.2423	-0.8698	-0.785	-0.7758	-0.5655	-0.486	-1.3955	-0.8372	-0.7182	0	0.005
2,5,7-NO2	-1.2425	-0.8748	-0.79	-0.7808	-0.5705	-0.4911	-1.4005	-0.8422	-0.7232	-0.005	0
2,5,8-NH2	-1.1832	0.7391	0.8239	0.8331	1.0434	1.1228	0.2134	0.7717	0.8907	1.6089	1.6139
2,5,8-OH	-1.207	0.0903	0.1751	0.1843	0.3946	0.4741	-0.4353	0.123	0.2419	0.9601	0.9652
2,5,8-CH3	-1.2133	-0.0826	0.0022	0.0114	0.2217	0.3012	-0.6083	-0.05	0.069	0.7872	0.7922
2,5,8-CN	-1.2397	-0.7997	-0.7149	-0.7057	-0.4954	-0.4159	-1.3253	-0.767	-0.6481	0.0701	0.0751
2,5,8-NO2	-1.2523	-1.1423	-1.0575	-1.0484	-0.838	-0.7586	-1.668	-1.1097	-0.9908	-0.2725	-0.2675
2,6,8-NH2	-1.1796	0.8345	0.9193	0.9284	1.1387	1.2182	0.3088	0.8671	0.986	1.7042	1.7093
2,6,8-OH	-1.206	0.1184	0.2032	0.2124	0.4227	0.5022	-0.4072	0.1511	0.27	0.9882	0.9932
2,6,8-CH3	-1.2152	-0.1324	-0.0476	-0.0385	0.1719	0.2513	-0.6581	-0.0998	0.0191	0.7374	0.7424
2,6,8-CN	-1.242	-0.8609	-0.7761	-0.767	-0.5566	-0.4772	-1.3866	-0.8283	-0.7094	0.0089	0.0139
2,6,8-NO2	-1.2551	-1.2181	-1.1333	-1.1241	-0.9138	-0.8343	-1.7438	-1.1855	-1.0665	-0.3483	-0.3433
Anthraquinones											
H	-1.1973	0.3531	0.438	0.4471	0.6574	0.7369	-0.1725	0.3858	0.5047	1.2229	1.228
1-NH2	-1.1756	0.9457	1.0305	1.0397	1.25	1.3295	0.42	0.9784	1.0973	1.8155	1.8205
1-OH	-1.1796	0.8363	0.9212	0.9303	1.1406	1.2201	0.3107	0.869	0.9879	1.7061	1.7112
1-CH3	-1.2184	-0.2206	-0.1358	-0.1267	0.0837	0.1631	-0.7463	-0.188	-0.0691	0.6492	0.6542
1-CN	-1.1908	0.5299	0.6147	0.6238	0.8342	0.9136	0.0042	0.5625	0.6814	1.3997	1.4047
1-NO2	-1.1927	0.4794	0.5642	0.5734	0.7837	0.8632	-0.0463	0.512	0.631	1.3492	1.3542
2-NH2	-1.1794	0.8408	0.9256	0.9347	1.145	1.2245	0.3151	0.8734	0.9923	1.7105	1.7156
2-OH	-1.1824	0.7603	0.8451	0.8543	1.0646	1.1441	0.2347	0.793	0.9119	1.6301	1.6351
2-CH3	-1.1827	0.7524	0.8372	0.8463	1.0566	1.1361	0.2267	0.785	0.9039	1.6221	1.6272
2-CN	-1.1915	0.5124	0.5972	0.6064	0.8167	0.8961	-0.0133	0.545	0.664	1.3822	1.3872
2-NO2	-1.1939	0.4455	0.5303	0.5395	0.7498	0.8292	-0.0802	0.4781	0.5971	1.3153	1.3203
1,3,5,7-NH2	-1.1639	1.2629	1.3477	1.3569	1.5672	1.6466	0.7372	1.2955	1.4144	2.1327	2.1377
1,3,5,7-OH	-1.1862	0.6574	0.7422	0.7514	0.9617	1.0412	0.1318	0.6901	0.809	1.5272	1.5323
1,3,5,7-CH3	-1.1871	0.6322	0.717	0.7262	0.9365	1.016	0.1065	0.6648	0.7838	1.502	1.507
1,3,5,7-CN	-1.2129	-0.0714	0.0134	0.0226	0.2329	0.3124	-0.5971	-0.0388	0.0802	0.7984	0.8034
1,3,5,7-NO2	-1.2216	-0.3065	-0.2217	-0.2125	-0.0022	0.0773	-0.8321	-0.2738	-0.1549	0.5633	0.5683

Table 3.6: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of napthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	2,5,8-NH2	2,5,8-OH	2,5,8-CH3	2,5,8-CN	2,5,8-NO2	2,6,8-NH2	2,6,8-OH	2,6,8-CH3	2,6,8-CN	2,6,8-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.1832	1.207	1.2133	1.2397	1.2523	1.1796	1.206	1.2152	1.242	1.2551
Benzoquinones											
H	-1.2437	-1.6464	-0.9976	-0.8247	-0.1076	0.2351	-1.7417	-1.0257	-0.7748	-0.0463	0.3108
2-NH2	-1.2248	-1.1341	-0.4854	-0.3125	0.4046	0.7473	-1.2295	-0.5135	-0.2626	0.4659	0.823
2-OH	-1.2275	-1.2069	-0.5581	-0.3852	0.3319	0.6745	-1.3023	-0.5862	-0.3354	0.3931	0.7503
2-CH3	-1.2325	-1.3436	-0.6948	-0.5219	0.1952	0.5379	-1.4389	-0.7229	-0.472	0.2565	0.6136
2-CN	-1.248	-1.7638	-1.1151	-0.9422	-0.2251	0.1176	-1.8592	-1.1432	-0.8923	-0.1638	0.1933
2-NO2	-1.2524	-1.8848	-1.236	-1.0631	-0.346	-0.0033	-1.9801	-1.2641	-1.0132	-0.2847	0.0724
2,5-NH2	-1.195	-0.3236	0.3252	0.4981	1.2152	1.5579	-0.4189	0.2971	0.548	1.2765	1.6336
2,5-OH	-1.2142	-0.8453	-0.1965	-0.0236	0.6935	1.0361	-0.9406	-0.2246	0.0262	0.7547	1.1119
2,5-CH3	-1.2273	-1.201	-0.5523	-0.3793	0.3378	0.6804	-1.2964	-0.5804	-0.3295	0.399	0.7562
2,5-CN	-1.2543	-1.9354	-1.2866	-1.1137	-0.3966	-0.054	-2.0308	-1.3147	-1.0639	-0.3354	0.0218
2,5-NO2	-1.2625	-2.1581	-1.5094	-1.3365	-0.6194	-0.2767	-2.2535	-1.5375	-1.2866	-0.5581	-0.201
Naphthoquinones											
H	-1.2256	-1.156	-0.5072	-0.3343	0.3828	0.7254	-1.2514	-0.5353	-0.2845	0.444	0.8012
2-NH2	-1.1993	-0.4387	0.21	0.3829	1.1	1.4427	-0.5341	0.1819	0.4328	1.1613	1.5184
2-OH	-1.2067	-0.6411	0.0077	0.1806	0.8977	1.2403	-0.7365	-0.0204	0.2304	0.9589	1.3161
2-CH3	-1.2105	-0.745	-0.0963	0.0766	0.7937	1.1364	-0.8404	-0.1244	0.1265	0.855	1.2121
2-CN	-1.2476	-1.7527	-1.104	-0.931	-0.2139	0.1287	-1.8481	-1.1321	-0.8812	-0.1527	0.2045
2-NO2	-1.2295	-1.2603	-0.6115	-0.4386	0.2785	0.6211	-1.3556	-0.6396	-0.3888	0.3397	0.6969
5-NH2	-1.2082	-0.6805	-0.0318	0.1412	0.8582	1.2009	-0.7759	-0.0599	0.191	0.9195	1.2767
5-OH	-1.2121	-0.7881	-0.1393	0.0336	0.7507	1.0933	-0.8834	-0.1674	0.0834	0.8119	1.1691
5-CH3	-1.2123	-0.7941	-0.1453	0.0276	0.7447	1.0873	-0.8894	-0.1734	0.0774	0.8059	1.1631
5-CN	-1.2191	-0.9784	-0.3296	-0.1567	0.5604	0.903	-1.0737	-0.3577	-0.1069	0.6216	0.9788
5-NO2	-1.2238	-1.1074	-0.4586	-0.2857	0.4314	0.774	-1.2028	-0.4867	-0.2359	0.4926	0.8498
6-NH2	-1.2103	-0.7391	-0.0903	0.0826	0.7997	1.1423	-0.8345	-0.1184	0.1324	0.8609	1.2181
6-OH	-1.2134	-0.8239	-0.1751	-0.0022	0.7149	1.0575	-0.9193	-0.2032	0.0476	0.7761	1.1333
6-CH3	-1.2138	-0.8331	-0.1843	-0.0114	0.7057	1.0484	-0.9284	-0.2124	0.0385	0.767	1.1241
6-CN	-1.2215	-1.0434	-0.3946	-0.2217	0.4954	0.838	-1.1387	-0.4227	-0.1719	0.5566	0.9138
6-NO2	-1.2244	-1.1228	-0.4741	-0.3012	0.4159	0.7586	-1.2182	-0.5022	-0.2513	0.4772	0.8343
2,5,7-NH2	-1.191	-0.2134	0.4353	0.6083	1.3253	1.668	-0.3088	0.4072	0.6581	1.3866	1.7438
2,5,7-OH	-1.2115	-0.7717	-0.123	0.05	0.767	1.1097	-0.8671	-0.1511	0.0998	0.8283	1.1855
2,5,7-CH3	-1.2159	-0.8907	-0.2419	-0.069	0.6481	0.9908	-0.986	-0.27	-0.0191	0.7094	1.0665
2,5,7-CN	-1.2423	-1.6089	-0.9601	-0.7872	-0.0701	0.2725	-1.7042	-0.9882	-0.7374	-0.0089	0.3483
2,5,7-NO2	-1.2425	-1.6139	-0.9652	-0.7922	-0.0751	0.2675	-1.7093	-0.9932	-0.7424	-0.0139	0.3433
2,5,8-NH2	-1.1832	0	0.6488	0.8217	1.5388	1.8814	-0.0954	0.6207	0.8715	1.6	1.9572
2,5,8-OH	-1.207	-0.6488	0	0.1729	0.89	1.2327	-0.7441	-0.0281	0.2228	0.9513	1.3084
2,5,8-CH3	-1.2133	-0.8217	-0.1729	0	0.7171	1.0597	-0.917	-0.201	0.0499	0.7784	1.1355
2,5,8-CN	-1.2397	-1.5388	-0.89	-0.7171	0	0.3427	-1.6341	-0.9181	-0.6672	0.0613	0.4184
2,5,8-NO2	-1.2523	-1.8814	-1.2327	-1.0597	-0.3427	0	-1.9768	-1.2608	-1.0099	-0.2814	0.0758
2,6,8-NH2	-1.1796	0.0954	0.7441	0.917	1.6341	1.9768	0	0.716	0.9669	1.6954	2.0525
2,6,8-OH	-1.206	-0.6207	0.0281	0.201	0.9181	1.2608	-0.716	0	0.2509	0.9794	1.3365
2,6,8-CH3	-1.2152	-0.8715	-0.2228	-0.0499	0.6672	1.0099	-0.9669	-0.2509	0	0.7285	1.0856
2,6,8-CN	-1.242	-1.6	-0.9513	-0.7784	-0.0613	0.2814	-1.6954	-0.9794	-0.7285	0	0.3571
2,6,8-NO2	-1.2551	-1.9572	-1.3084	-1.1355	-0.4184	-0.0758	-2.0525	-1.3365	-1.0856	-0.3571	0
Anthraquinones											
H	-1.1973	-0.3859	0.2628	0.4357	1.1528	1.4955	-0.4813	0.2347	0.4856	1.2141	1.5712
1-NH2	-1.1756	0.2066	0.8554	1.0283	1.7454	2.0881	0.1113	0.8273	1.0782	1.8067	2.1638
1-OH	-1.1796	0.0973	0.746	0.9189	1.636	1.9787	0.0019	0.7179	0.9688	1.6973	2.0544
1-CH3	-1.2184	-0.9597	-0.311	-0.1381	0.579	0.9217	-1.0551	-0.3391	-0.0882	0.6403	0.9974
1-CN	-1.1908	-0.2092	0.4395	0.6124	1.3295	1.6722	-0.3046	0.4114	0.6623	1.3908	1.7479
1-NO2	-1.1927	-0.2597	0.3891	0.562	1.2791	1.6217	-0.3551	0.361	0.6118	1.3403	1.6975
2-NH2	-1.1794	0.1017	0.7504	0.9233	1.6404	1.9831	0.0063	0.7223	0.9732	1.7017	2.0588
2-OH	-1.1824	0.0212	0.67	0.8429	1.56	1.9027	-0.0741	0.6419	0.8928	1.6213	1.9784
2-CH3	-1.1827	0.0133	0.662	0.8349	1.552	1.8947	-0.0821	0.6339	0.8848	1.6133	1.9704
2-CN	-1.1915	-0.2267	0.4221	0.595	1.3121	1.6547	-0.3221	0.394	0.6448	1.3733	1.7305
2-NO2	-1.1939	-0.2936	0.3552	0.5281	1.2452	1.5878	-0.389	0.3271	0.5779	1.3064	1.6636
1,3,5,7-NH2	-1.1639	0.5238	1.1725	1.3455	2.0626	2.4052	0.4284	1.1445	1.3953	2.1238	2.481
1,3,5,7-OH	-1.1862	-0.0816	0.5671	0.74	1.4571	1.7998	-0.177	0.539	0.7899	1.5184	1.8755
1,3,5,7-CH3	-1.1871	-0.1069	0.5419	0.7148	1.4319	1.7745	-0.2022	0.5138	0.7646	1.4931	1.8503
1,3,5,7-CN	-1.2129	-0.8105	-0.1617	0.0112	0.7283	1.0709	-0.9058	-0.1898	0.061	0.7895	1.1467
1,3,5,7-NO2	-1.2216	-1.0456	-0.3968	-0.2239	0.4932	0.8359	-1.1409	-0.4249	-0.174	0.5545	0.9116

Table 3.7: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised AH_2Q	H	1-NH2	1-OH	1-CH3	1-CN	1-NO2	2-NH2	2-OH	2-CH3	2-CN	2-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.1973	1.1756	1.1796	1.2184	1.1908	1.1927	1.1794	1.1824	1.1827	1.1915	1.1939
Benzoquinones												
H	-1.2437	-1.2604	-1.853	-1.7436	-0.6866	-1.4371	-1.3867	-1.748	-1.6676	-1.6596	-1.4197	-1.3528
2-NH2	-1.2248	-0.7482	-1.3408	-1.2314	-0.1744	-0.9249	-0.8744	-1.2358	-1.1554	-1.1474	-0.9074	-0.8405
2-OH	-1.2275	-0.821	-1.4135	-1.3042	-0.2472	-0.9977	-0.9472	-1.3086	-1.2281	-1.2202	-0.9802	-0.9133
2-CH3	-1.2325	-0.9576	-1.5502	-1.4408	-0.3838	-1.1343	-1.0839	-1.4452	-1.3648	-1.3568	-1.1169	-1.05
2-CN	-1.248	-1.3779	-1.9705	-1.8611	-0.8041	-1.5546	-1.5042	-1.8655	-1.7851	-1.7771	-1.5371	-1.4702
2-NO2	-1.2524	-1.4988	-2.0914	-1.982	-0.925	-1.6755	-1.6251	-1.9864	-1.906	-1.898	-1.6581	-1.5912
2,5-NH2	-1.195	0.0624	-0.5302	-0.4208	0.6362	-0.1143	-0.0639	-0.4252	-0.3448	-0.3368	-0.0969	-0.03
2,5-OH	-1.2142	-0.4593	-1.0519	-0.9425	0.1144	-0.6361	-0.5856	-0.9469	-0.8665	-0.8585	-0.6186	-0.5517
2,5-CH3	-1.2273	-0.8151	-1.4076	-1.2983	-0.2413	-0.9918	-0.9413	-1.3027	-1.2223	-1.2143	-0.9743	-0.9074
2,5-CN	-1.2543	-1.5495	-2.142	-2.0327	-0.9757	-1.7262	-1.6757	-2.0371	-1.9566	-1.9487	-1.7087	-1.6418
2,5-NO2	-1.2625	-1.7722	-2.3648	-2.2554	-1.1984	-1.9489	-1.8984	-2.2598	-2.1794	-2.1714	-1.9314	-1.8645
Naphthoquinones												
H	-1.2256	-0.77	-1.3626	-1.2533	-0.1963	-0.9468	-0.8963	-1.2577	-1.1772	-1.1693	-0.9293	-0.8624
2-NH2	-1.1993	-0.0528	-0.6454	-0.536	0.521	-0.2295	-0.1791	-0.5404	-0.46	-0.452	-0.212	-0.1451
2-OH	-1.2067	-0.2552	-0.8477	-0.7384	0.3186	-0.4319	-0.3814	-0.7428	-0.6623	-0.6544	-0.4144	-0.3475
2-CH3	-1.2105	-0.3591	-0.9517	-0.8423	0.2147	-0.5358	-0.4854	-0.8467	-0.7663	-0.7583	-0.5183	-0.4514
2-CN	-1.2476	-1.3668	-1.9593	-1.85	-0.793	-1.5435	-1.493	-1.8544	-1.774	-1.766	-1.526	-1.4591
2-NO2	-1.2295	-0.8743	-1.4669	-1.3575	-0.3006	-1.0511	-1.0006	-1.3619	-1.2815	-1.2735	-1.0336	-0.9667
5-NH2	-1.2082	-0.2946	-0.8871	-0.7778	0.2792	-0.4713	-0.4208	-0.7822	-0.7018	-0.6938	-0.4538	-0.3869
5-OH	-1.2121	-0.4021	-0.9947	-0.8853	0.1716	-0.5789	-0.5284	-0.8897	-0.8093	-0.8013	-0.5614	-0.4945
5-CH3	-1.2123	-0.4081	-1.0007	-0.8913	0.1656	-0.5849	-0.5344	-0.8958	-0.8153	-0.8073	-0.5674	-0.5005
5-CN	-1.2191	-0.5924	-1.185	-1.0756	-0.0187	-0.7692	-0.7187	-1.0801	-0.9996	-0.9916	-0.7517	-0.6848
5-NO2	-1.2238	-0.7214	-1.314	-1.2046	-0.1477	-0.8982	-0.8477	-1.2091	-1.1286	-1.1207	-0.8807	-0.8138
6-NH2	-1.2103	-0.3531	-0.9457	-0.8363	0.2206	-0.5299	-0.4794	-0.8408	-0.7603	-0.7524	-0.5124	-0.4455
6-OH	-1.2134	-0.438	-1.0305	-0.9212	0.1358	-0.6147	-0.5642	-0.9256	-0.8451	-0.8372	-0.5972	-0.5303
6-CH3	-1.2138	-0.4471	-1.0397	-0.9303	0.1267	-0.6238	-0.5734	-0.9347	-0.8543	-0.8463	-0.6064	-0.5395
6-CN	-1.2215	-0.6574	-1.25	-1.1406	-0.0837	-0.8342	-0.7837	-1.145	-1.0646	-1.0566	-0.8167	-0.7498
6-NO2	-1.2244	-0.7369	-1.3295	-1.2201	-0.1631	-0.9136	-0.8632	-1.2245	-1.1441	-1.1361	-0.8961	-0.8292
2,5,7-NH2	-1.191	0.1725	-0.42	-0.3107	0.7463	-0.0042	0.0463	-0.3151	-0.2347	-0.2267	0.0133	0.0802
2,5,7-OH	-1.2115	-0.3858	-0.9784	-0.869	0.188	-0.5625	-0.512	-0.8734	-0.793	-0.785	-0.545	-0.4781
2,5,7-CH3	-1.2159	-0.5047	-1.0973	-0.9879	0.0691	-0.6814	-0.631	-0.9923	-0.9119	-0.9039	-0.664	-0.5971
2,5,7-CN	-1.2423	-1.2229	-1.8155	-1.7061	-0.6492	-1.3997	-1.3492	-1.7105	-1.6301	-1.6221	-1.3822	-1.3153
2,5,7-NO2	-1.2425	-1.228	-1.8205	-1.7112	-0.6542	-1.4047	-1.3542	-1.7156	-1.6351	-1.6272	-1.3872	-1.3203
2,5,8-NH2	-1.1832	0.3859	-0.2066	-0.0973	0.9597	0.2092	0.2597	-0.1017	-0.0212	-0.0133	0.2267	0.2936
2,5,8-OH	-1.207	-0.2628	-0.8554	-0.746	0.311	-0.4395	-0.3891	-0.7504	-0.67	-0.662	-0.4221	-0.3552
2,5,8-CH3	-1.2133	-0.4357	-1.0283	-0.9189	0.1381	-0.6124	-0.562	-0.9233	-0.8429	-0.8349	-0.595	-0.5281
2,5,8-CN	-1.2397	-1.1528	-1.7454	-1.636	-0.579	-1.3295	-1.2791	-1.6404	-1.56	-1.552	-1.3121	-1.2452
2,5,8-NO2	-1.2523	-1.4955	-2.0881	-1.9787	-0.9217	-1.6722	-1.6217	-1.9831	-1.9027	-1.8947	-1.6547	-1.5878
2,6,8-NH2	-1.1796	0.4813	-0.1113	-0.0019	1.0551	0.3046	0.3551	-0.0063	0.0741	0.0821	0.3221	0.389
2,6,8-OH	-1.206	-0.2347	-0.8273	-0.7179	0.3391	-0.4114	-0.361	-0.7223	-0.6419	-0.6339	-0.394	-0.3271
2,6,8-CH3	-1.2152	-0.4856	-1.0782	-0.9688	0.0882	-0.6623	-0.6118	-0.9732	-0.8928	-0.8848	-0.6448	-0.5779
2,6,8-CN	-1.242	-1.2141	-1.8067	-1.6973	-0.6403	-1.3908	-1.3403	-1.7017	-1.6213	-1.6133	-1.3733	-1.3064
2,6,8-NO2	-1.2551	-1.5712	-2.1638	-2.0544	-0.9974	-1.7479	-1.6975	-2.0588	-1.9784	-1.9704	-1.7305	-1.6636
Anthraquinones												
H	-1.1973	0	-0.5926	-0.4832	0.5738	-0.1767	-0.1263	-0.4876	-0.4072	-0.3992	-0.1592	-0.0923
1-NH2	-1.1756	0.5926	0	0.1094	1.1664	0.4159	0.4663	0.105	0.1854	0.1934	0.4333	0.5002
1-OH	-1.1796	0.4832	-0.1094	0	1.057	0.3065	0.3569	-0.0044	0.076	0.084	0.324	0.3909
1-CH3	-1.2184	-0.5738	-1.1664	-1.057	0	-0.7505	-0.7	-1.0614	-0.981	-0.973	-0.733	-0.6661
1-CN	-1.1908	0.1767	-0.4159	-0.3065	0.7505	0	0.0505	-0.3109	-0.2305	-0.2225	0.0175	0.0844
1-NO2	-1.1927	0.1263	-0.4663	-0.3569	0.7	-0.0505	0	-0.3614	-0.2809	-0.2729	-0.033	0.0339
2-NH2	-1.1794	0.4876	-0.105	0.0044	1.0614	0.3109	0.3614	0	0.0804	0.0884	0.3284	0.3953
2-OH	-1.1824	0.4072	-0.1854	-0.076	0.981	0.2305	0.2809	-0.0804	0	0.008	0.2479	0.3148
2-CH3	-1.1827	0.3992	-0.1934	-0.084	0.973	0.2225	0.2729	-0.0884	-0.008	0	0.24	0.3069
2-CN	-1.1915	0.1592	-0.4333	-0.324	0.733	-0.0175	0.033	-0.3284	-0.2479	-0.24	0	0.0669
2-NO2	-1.1939	0.0923	-0.5002	-0.3909	0.6661	-0.0844	-0.0339	-0.3953	-0.3148	-0.3069	-0.0669	0
1,3,5,7-NH2	-1.1639	0.9097	0.3172	0.4265	1.4835	0.733	0.7835	0.4221	0.5025	0.5105	0.7505	0.8174
1,3,5,7-OH	-1.1862	0.3043	-0.2883	-0.1789	0.8781	0.1276	0.178	-0.1833	-0.1029	-0.0949	0.145	0.2119
1,3,5,7-CH3	-1.1871	0.2791	-0.3135	-0.2041	0.8528	0.1023	0.1528	-0.2085	-0.1281	-0.1201	0.1198	0.1867
1,3,5,7-CN	-1.2129	-0.4245	-1.0171	-0.9077	0.1492	-0.6013	-0.5508	-0.9121	-0.8317	-0.8237	-0.5838	-0.5169
1,3,5,7-NO2	-1.2216	-0.6596	-1.2522	-1.1428	-0.0858	-0.8363	-0.7859	-1.1472	-1.0668	-1.0588	-0.8189	-0.752

Table 3.8: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised AH_2Q	1,3,5,7-NH2	1,3,5,7-OH	1,3,5,7-CH3	1,3,5,7-CN	1,3,5,7-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.1639	1.1862	1.1871	1.2129	1.2216
Benzoquinones						
H	-1.2437	-2.1702	-1.5647	-1.5395	-0.8359	-0.6008
2-NH2	-1.2248	-1.6579	-1.0525	-1.0273	-0.3237	-0.0886
2-OH	-1.2275	-1.7307	-1.1252	-1.1	-0.3964	-0.1613
2-CH3	-1.2325	-1.8674	-1.2619	-1.2367	-0.5331	-0.298
2-CN	-1.248	-2.2876	-1.6822	-1.657	-0.9534	-0.7183
2-NO2	-1.2524	-2.4085	-1.8031	-1.7779	-1.0743	-0.8392
2,5-NH2	-1.195	-0.8474	-0.2419	-0.2167	0.4869	0.722
2,5-OH	-1.2142	-1.3691	-0.7636	-0.7384	-0.0348	0.2003
2,5-CH3	-1.2273	-1.7248	-1.1194	-1.0941	-0.3905	-0.1555
2,5-CN	-1.2543	-2.4592	-1.8537	-1.8285	-1.1249	-0.8898
2,5-NO2	-1.2625	-2.6819	-2.0765	-2.0512	-1.3476	-1.1126
Naphthoquinones						
H	-1.2256	-1.6798	-1.0743	-1.0491	-0.3455	-0.1104
2-NH2	-1.1993	-0.9625	-0.3571	-0.3319	0.3717	0.6068
2-OH	-1.2067	-1.1649	-0.5594	-0.5342	0.1694	0.4045
2-CH3	-1.2105	-1.2688	-0.6634	-0.6382	0.0654	0.3005
2-CN	-1.2476	-2.2765	-1.6711	-1.6458	-0.9422	-0.7072
2-NO2	-1.2295	-1.7841	-1.1786	-1.1534	-0.4498	-0.2147
5-NH2	-1.2082	-1.2043	-0.5989	-0.5736	0.13	0.365
5-OH	-1.2121	-1.3119	-0.7064	-0.6812	0.0224	0.2575
5-CH3	-1.2123	-1.3179	-0.7124	-0.6872	0.0164	0.2515
5-CN	-1.2191	-1.5022	-0.8967	-0.8715	-0.1679	0.0672
5-NO2	-1.2238	-1.6312	-1.0257	-1.0005	-0.2969	-0.0618
6-NH2	-1.2103	-1.2629	-0.6574	-0.6322	0.0714	0.3065
6-OH	-1.2134	-1.3477	-0.7422	-0.717	-0.0134	0.2217
6-CH3	-1.2138	-1.3569	-0.7514	-0.7262	-0.0226	0.2125
6-CN	-1.2215	-1.5672	-0.9617	-0.9365	-0.2329	0.0022
6-NO2	-1.2244	-1.6466	-1.0412	-1.016	-0.3124	-0.0773
2,5,7-NH2	-1.191	-0.7372	-0.1318	-0.1065	0.5971	0.8321
2,5,7-OH	-1.2115	-1.2955	-0.6901	-0.6648	0.0388	0.2738
2,5,7-CH3	-1.2159	-1.4144	-0.809	-0.7838	-0.0802	0.1549
2,5,7-CN	-1.2423	-2.1327	-1.5272	-1.502	-0.7984	-0.5633
2,5,7-NO2	-1.2425	-2.1377	-1.5323	-1.507	-0.8034	-0.5683
2,5,8-NH2	-1.1832	-0.5238	0.0816	0.1069	0.8105	1.0456
2,5,8-OH	-1.207	-1.1725	-0.5671	-0.5419	0.1617	0.3968
2,5,8-CH3	-1.2133	-1.3455	-0.74	-0.7148	-0.0112	0.2239
2,5,8-CN	-1.2397	-2.0626	-1.4571	-1.4319	-0.7283	-0.4932
2,5,8-NO2	-1.2523	-2.4052	-1.7998	-1.7745	-1.0709	-0.8359
2,6,8-NH2	-1.1796	-0.4284	0.177	0.2022	0.9058	1.1409
2,6,8-OH	-1.206	-1.1445	-0.539	-0.5138	0.1898	0.4249
2,6,8-CH3	-1.2152	-1.3953	-0.7899	-0.7646	-0.061	0.174
2,6,8-CN	-1.242	-2.1238	-1.5184	-1.4931	-0.7895	-0.5545
2,6,8-NO2	-1.2551	-2.481	-1.8755	-1.8503	-1.1467	-0.9116
Anthraquinones						
H	-1.1973	-0.9097	-0.3043	-0.2791	0.4245	0.6596
1-NH2	-1.1756	-0.3172	0.2883	0.3135	1.0171	1.2522
1-OH	-1.1796	-0.4265	0.1789	0.2041	0.9077	1.1428
1-CH3	-1.2184	-1.4835	-0.8781	-0.8528	-0.1492	0.0858
1-CN	-1.1908	-0.733	-0.1276	-0.1023	0.6013	0.8363
1-NO2	-1.1927	-0.7835	-0.178	-0.1528	0.5508	0.7859
2-NH2	-1.1794	-0.4221	0.1833	0.2085	0.9121	1.1472
2-OH	-1.1824	-0.5025	0.1029	0.1281	0.8317	1.0668
2-CH3	-1.1827	-0.5105	0.0949	0.1201	0.8237	1.0588
2-CN	-1.1915	-0.7505	-0.145	-0.1198	0.5838	0.8189
2-NO2	-1.1939	-0.8174	-0.2119	-0.1867	0.5169	0.752
1,3,5,7-NH2	-1.1639	0	0.6054	0.6307	1.3343	1.5693
1,3,5,7-OH	-1.1862	-0.6054	0	0.0252	0.7288	0.9639
1,3,5,7-CH3	-1.1871	-0.6307	-0.0252	0	0.7036	0.9387
1,3,5,7-CN	-1.2129	-1.3343	-0.7288	-0.7036	0	0.2351
1,3,5,7-NO2	-1.2216	-1.5693	-0.9639	-0.9387	-0.2351	0

Thirty-one pairs of redox couples store at least 2.0 eV. These all comprise a quinone with electron-donating groups and a hydroquinone with electron-withdrawing groups. In particular, 1,3,5,7-NH_2AQ features as one half of many of these pairs as a large, electron-rich quinone which requires a lot of energy to reduce. The electron-poor hydroquinones 2,5-CNBH_2Q, 2,5-NO_2BH_2Q and 2,6,8-NO_2NH_2Q require a lot of energy to oxidise, and are the oxidised species in many of the pairs storing greater than 2.0 eV.

3.3.4 Combined effect of ring system size and substitution on photorechargeability

The two goals of increasing $\Delta E_{\mathrm{stored}}$ and optimising ΔE_1 and ΔE_2 are, to an extent, opposing; increasing the amount of energy stored will generally increase the heights of energy barriers. The aim of this work is therefore to strike a balance between a high $\Delta E_{\mathrm{stored}}$ and desirable values of ΔE_1 and ΔE_2 and identify the pairs of quinones which provide this balance.

Tables B.19 to B.24 give the P value for each possible cell, as defined in Equation 3.1. The tables are laid out with quinones becoming more substituted left-to-right and top-to-bottom. In each block of five, the substituents are ordered from most electron-donating (NH_2) to most electron-withdrawing (NO_2). There is no clear trend in which substituents are the best for photorechargeability. However, some quinone half-cells feature prominently with high P values. A P value of 0 indicates that the cell does not store energy. A "—" indicates that one or both of the barrier heights is significantly outside the range of 0.5–2.5 eV and have low f_{SQ} values.

Table 3.9: P (eV) for coupled redox reactions involving oxidation of benzohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised BH_2Q	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	2,5-NH_2	2,5-OH	2,5-CH_3	2,5-CN	2,5-NO_2
Reduced quinone											
Benzoquinones											
H	—	—	—	—	0.0085	0.0128	—	—	—	0.0084	0.0079
2-NH_2	0	—	0	0	0	0	—	—	0	0	0
2-OH	0.1028	—	—	0.0209	0.0346	0.0309	—	—	—	0.0173	0.0147
2-CH_3	0	—	—	—	0	0	—	—	—	0	0
2-CN	—	—	—	—	—	0	—	—	—	0.0052	0.0414
2-NO_2	—	—	—	—	—	—	—	—	—	0.0047	0.0493
2,5-NH_2	0	0	0	0	0	0	—	0	0	0	0
2,5-OH	0	0	0	0	0	0	—	—	0	0	0
2,5-CH_3	0	—	0	0	0	0	—	—	—	0	0
2,5-CN	—	—	—	—	—	—	—	—	—	—	0.0552
2,5-NO_2	—	—	—	—	—	—	—	—	—	—	—
Naphthoquinones											
H	0.0883	0	0.0069	0.0196	0.0226	0.0173	0	0	0.0061	0.0089	0.0053
2-NH_2	0.2070	0.1423	0.1036	0.0948	0.0384	0.0344	0	0.0660	0.1028	0.0170	0.0091
2-OH	0.2210	0.1283	0.0970	0.1011	0.0697	0.0567	0	0.0433	0.1009	0.0308	0.0173
2-CH_3	0.1545	0.1076	0.0871	0.0972	0.0736	0.0612	0	0.0228	0.0897	0.0283	0.0218
2-CN	0	0	0	0	0.0019	0.0190	—	0	0	0.0172	0.0252
2-NO_2	0.0926	0	0	0.0273	0.1499	0.1695	—	0	0	0.1433	0.1617
5-NH_2	0.1900	0.1296	0.1035	0.1137	0.0783	0.0647	0	0.0397	0.1065	0.0364	0.0228
5-OH	0.1618	0.0999	0.0889	0.1001	0.0811	0.0681	0	0.0142	0.0876	0.0333	0.0271
5-CH_3	0.1535	0.0940	0.0778	0.0893	0.0701	0.0586	0	0.0116	0.0800	0.0271	0.0211
5-CN	0.1563	0.0501	0.0580	0.0830	0.1059	0.0851	0	0	0.0579	0.0514	0.0342
5-NO_2	0.1603	0.0048	0.0305	0.0727	0.1815	0.1925	—	0	0.0278	0.1628	0.1610
6-NH_2	0.1474	0.0978	0.0760	0.0815	0.0550	0.0426	0	0.0209	0.0750	0.0237	0.0162
6-OH	0.1551	0.0923	0.0842	0.0980	0.0883	0.0767	0	0.0056	0.0829	0.0413	0.0264
6-CH_3	0.1465	0.0848	0.0735	0.0875	0.0673	0.0565	0	0.0029	0.0724	0.0320	0.0205
6-CN	0.1453	0.0293	0.0444	0.0723	0.1037	0.0966	0	0	0.0436	0.0645	0.0509
6-NO_2	0.1577	0.0035	0.0253	0.0622	0.1155	0.1167	0	0	0.0239	0.0851	0.0643
2,5,7-NH_2	0.0415	0.0420	0.0154	0.0129	0.0014	0.0002	0.0148	0.0150	0.0196	0	0
2,5,7-OH	0.0727	0.0416	0.0234	0.0212	0.0081	0.0059	0	0.0053	0.0230	0.0011	0
2,5,7-CH_3	0.1019	0.0373	0.0229	0.0243	0.0135	0.0113	0	0	0.0258	0.0029	0.0012
2,5,7-CN	0.0120	0	0	0	0.0317	0.0473	—	0	0	0.0440	0.0457
2,5,7-NO_2	0.0101	0	0	0	0.0361	0.0575	—	0	0	0.0522	0.0625
2,5,8-NH_2	0.0477	0.0517	0.0187	0.0153	0.0002	0	0.0436	0.0201	0.0186	0	0
2,5,8-OH	0.0721	0.0508	0.0255	0.0201	0.0091	0.0034	0	0.0122	0.0252	0.0002	0
2,5,8-CH_3	0.0947	0.0450	0.0278	0.0280	0.0146	0.0087	0	0.0025	0.0274	0.0031	0.0012
2,5,8-CN	0.0356	0	0	0	0.0424	0.0530	—	0	0	0.0415	0.0448
2,5,8-NO_2	0	0	0	0	0	0.0006	—	0	0	0.0073	0.0260
2,6,8-NH_2	0.0505	0.0561	0.0201	0.0164	0.0017	0.0002	0.0565	0.0224	0.0257	0	0
2,6,8-OH	0.0853	0.0538	0.0267	0.0210	0.0093	0.0067	0	0.0162	0.0265	0.0012	0
2,6,8-CH_3	0.0890	0.0402	0.0242	0.0253	0.0138	0.0115	0	0	0.0274	0.0030	0.0012
2,6,8-CN	0.0154	0	0	0	0.0295	0.0436	—	0	0	0.0351	0.0403
2,6,8-NO_2	0	0	0	0	0	0	—	0	0	0	0.0189
Anthraquinones											
H	0.1699	0.1700	0.1181	0.1099	0.0512	0.0435	0	0.0827	0.1173	0.0240	0.0145
1-NH_2	0.2666	0.3707	0.2780	0.2519	0.1424	0.1123	0.1639	0.2462	0.2768	0.0621	0.0366
1-OH	0.2350	0.3342	0.2459	0.2596	0.1345	0.1064	0.1374	0.2334	0.2656	0.0483	0.0349
1-CH_3	0.1655	0.0423	0.0466	0.0624	0.0581	0.0497	—	0	0.0475	0.0232	0.0185
1-CN	0.2826	0.2860	0.2335	0.2321	0.1628	0.1393	0.0282	0.1758	0.2390	0.0788	0.0463
1-NO_2	0.4247	0.2156	0.3065	0.3494	0.4009	0.3803	0.0014	0.1781	0.3074	0.3019	0.2559
2-NH_2	0.1831	0.3060	0.2126	0.2079	0.1002	0.0738	0.1370	0.2010	0.2233	0.0403	0.0257
2-OH	0.2248	0.3006	0.2212	0.2217	0.1108	0.0870	0.1123	0.2088	0.2305	0.0465	0.0337
2-CH_3	0.3130	0.3114	0.2301	0.2204	0.1103	0.0866	0.0854	0.1950	0.2290	0.0463	0.0336
2-CN	0.3783	0.2836	0.2362	0.2370	0.1765	0.1378	0.0145	0.1710	0.2413	0.0780	0.0560
2-NO_2	0.1824	0.2281	0.1722	0.1891	0.1062	0.0854	0.0072	0.1400	0.1857	0.0390	0.0288
1,3,5,7-NH_2	0.0516	0.0756	0.0268	0.0213	0.0021	0.0003	0.1142	0.0326	0.0267	0	0
1,3,5,7-OH	0.0840	0.0988	0.0418	0.0300	0.0089	0.0050	0.0476	0.0410	0.0416	0.0002	0
1,3,5,7-CH_3	0.1112	0.1385	0.0591	0.0459	0.0135	0.0094	0.0492	0.0614	0.0587	0.0017	0
1,3,5,7-CN	0.2517	0.0991	0.1096	0.1320	0.1372	0.1233	0	0.0106	0.1100	0.0813	0.0615
1,3,5,7-NO_2	0.1947	0.0216	0.0499	0.0861	0.1354	0.1286	—	0	0.0486	0.0932	0.0804

Table 3.10: P (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised {NH2Q}	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	5-NH_2	5-OH	5-CH_3	5-CN	5-NO_2
Reduced quinone											
Benzoquinones											
H	0	0	0	0	0.0304	0	0	0	0	0	0
2-NH_2	—	—	—	—	—	—	—	—	—	—	—
2-OH	0	0	0	0	0.1455	0.0145	0	0	0	0	0
2-CH_3	—	—	—	—	—	—	—	—	—	—	—
2-CN	—	—	—	—	—	—	—	—	—	—	—
2-NO_2	—	—	—	—	—	—	—	—	—	—	—
2,5-NH_2	—	—	—	—	—	—	—	—	—	—	—
2,5-OH	—	—	—	—	—	—	—	—	—	—	—
2,5-CH_3	—	—	—	—	—	—	—	—	—	—	—
2,5-CN	—	—	—	—	—	—	—	—	—	—	—
2,5-NO_2	—	—	—	—	—	—	—	—	—	—	—
Naphthoquinones											
H	0	0	0	0	0.1174	0.0213	0	0	0	0	0
2-NH_2	0.1468	0	0.0626	0.0885	0.2367	0.1549	0.0782	0.1115	0.1058	0.1145	0.2123
2-OH	0.1306	0	0	0.0334	0.2601	0.1492	0.0120	0.0472	0.0498	0.0878	0.1429
2-CH_3	0.0841	0	0	0	0.1815	0.1013	0	0.0137	0.0146	0.0495	0.1098
2-CN	0	—	0	0	0	0	—	0	0	0	0
2-NO_2	0	—	—	—	0.0830	0	—	—	—	0	—
5-NH_2	0.1113	0	0	0.0199	0.2275	0.1275	0	0.0332	0.0361	0.0718	0.1201
5-OH	0.0809	0	0	0	0.1897	0.1002	0	0	0.0019	0.0432	0.0818
5-CH_3	0.0768	0	0	0	0.1808	0.0917	0	0	0	0.0405	0.0950
5-CN	0.0473	0	0	0	0.1918	0.0715	0	0	0	0	0.0256
5-NO_2	0.0113	—	—	0	0.1530	0.0288	—	—	0	0	—
6-NH_2	0.0820	0	0	0.0017	0.1737	0.0983	0	0.0156	0.0161	0.0490	0.1152
6-OH	0.0754	0	0	0	0.1901	0.0926	0	0	0	0.0362	0.0691
6-CH_3	0.0710	0	0	0	0.1809	0.0874	0	0	0	0.0330	0.0806
6-CN	0.0311	0	0	0	0.1800	0.0578	0	0	0	0	0.0108
6-NO_2	0.0107	—	0	0	0.1947	0.0426	0	0	0	0	0
2,5,7-NH_2	0.0506	0.0586	0.0806	0.0814	0.0826	0.0650	0.0956	0.0985	0.0835	0.0553	0.1829
2,5,7-OH	0.0518	0	0	0	0.1322	0.0703	0	0.0043	0.0052	0.0317	0.0969
2,5,7-CH_3	0.0406	0	0	0	0.1162	0.0532	0	0	0	0.0143	0.0619
2,5,7-CN	0	—	0	0	0.0446	0	0	0	0	0	0
2,5,7-NO_2	0	—	0	0	0.0379	0	—	0	0	0	—
2,5,8-NH_2	0.0621	0.0997	0.1099	0.1072	0.0800	0.0782	0.1338	0.1280	0.1070	0.0607	0.2088
2,5,8-OH	0.0582	0	0	0.0225	0.1268	0.0824	0.0089	0.0345	0.0320	0.0444	0.1268
2,5,8-CH_3	0.0512	0	0	0	0.1255	0.0591	0	0	0	0.0240	0.0790
2,5,8-CN	0	—	0	0	0.0704	0	0	0	0	0	0
2,5,8-NO_2	0	—	0	0	0	0	0	0	0	0	0
2,6,8-NH_2	0.0672	0.1133	0.1197	0.1133	0.0843	0.0728	0.1588	0.1435	0.1280	0.0666	0.2062
2,6,8-OH	0.0615	0	0.0053	0.0291	0.1300	0.0862	0.0171	0.0415	0.0381	0.0515	0.1346
2,6,8-CH_3	0.0436	0	0	0	0.1188	0.0559	0	0	0	0.0174	0.0674
2,6,8-CN	0	—	0	0	0.0502	0	0	0	0	0	0
2,6,8-NO_2	0	—	0	0	0	0	0	0	0	0	0
Anthraquinones											
H	0.1251	0.0128	0.0705	0.0911	0.1967	0.1339	0.0969	0.1178	0.1088	0.1016	0.2084
1-NH_2	0.2455	0.1056	0.2484	0.2583	0.3183	0.2514	0.2569	0.3037	0.2818	0.2235	0.3909
1-OH	0.2148	0.0737	0.2080	0.2191	0.2662	0.2080	0.1992	0.2635	0.2419	0.1938	0.3161
1-CH_3	0.0561	0	0	0	0.2233	0.0905	0	0	0	0.0056	0.0312
1-CN	0.2216	0.0169	0.1052	0.1624	0.3275	0.2311	0.1106	0.1605	0.1793	0.1853	0.2125
1-NO_2	0.2160	—	—	0.0142	0.3630	0.2258	—	0.0085	0.0283	0.1472	—
2-NH_2	0.1810	0.1072	0.1932	0.1981	0.2500	0.1836	0.2397	0.2460	0.2159	0.1655	0.3282
2-OH	0.1913	0.0673	0.1798	0.1898	0.2391	0.1844	0.1841	0.2337	0.2121	0.1624	0.3085
2-CH_3	0.2656	0.0781	0.2011	0.2315	0.3613	0.2703	0.2103	0.2635	0.2549	0.2321	0.3413
2-CN	0.2766	0.0147	0.1006	0.1555	0.4219	0.2952	0.1047	0.1513	0.1738	0.2264	0.2059
2-NO_2	0.1478	—	0.0538	0.0944	0.2099	0.1481	0.0420	0.0896	0.1186	0.1234	0.0942
1,3,5,7-NH_2	0.0624	0.1734	0.1570	0.1329	0.0660	0.0517	0.2464	0.1768	0.1380	0.0685	0.2199
1,3,5,7-OH	0.0776	0.0836	0.1008	0.1016	0.1037	0.0732	0.1596	0.1389	0.1157	0.0745	0.2017
1,3,5,7-CH_3	0.1099	0.0901	0.1134	0.1203	0.1368	0.1083	0.1681	0.1548	0.1352	0.0913	0.2273
1,3,5,7-CN	0.1111	0	0	0	0.2913	0.1420	0	0	0	0.0548	0.0479
1,3,5,7-NO_2	0.0356	—	0	0	0.2328	0.0660	0	0	0	0	0.0045

Table 3.11: P (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised NH_2Q	6-NH_2	6-OH	6-CH_3	6-CN	6-NO_2	2,5,7-NH_2	2,5,7-OH	2,5,7-CH_3	2,5,7-CN	2,5,7-NO_2
Reduced quinone										
Benzoquinones										
H	0	0	0	0	0	0	0	0	0	0
2-NH_2	—	—	—	—	—	—	—	—	—	—
2-OH	0	0	0	0	0	0	0	0	0.0290	0.0219
2-CH_3	—	—	—	—	—	—	—	—	—	—
2-CN	—	—	—	—	—	—	—	—	—	—
2-NO_2	—	—	—	—	—	—	—	—	—	—
2,5-NH_2	—	—	—	—	—	—	—	—	—	—
2,5-OH	—	—	—	—	—	—	—	—	—	—
2,5-CH_3	—	—	—	—	—	—	—	—	—	—
2,5-CN	—	—	—	—	—	—	—	—	0	0
2,5-NO_2	—	—	—	—	—	—	—	—	0	0
Naphthoquinones										
H	0	0	0	0	0	0	0	0	0.0207	0.0109
2-NH_2	0.0985	0.1160	0.1126	0.1237	0.1601	0	0.0887	0.1147	0.0435	0.0233
2-OH	0.0296	0.0605	0.0613	0.1021	0.1357	0	0.0399	0.0752	0.0601	0.0361
2-CH_3	0	0.0238	0.0254	0.0610	0.0884	0	0.0071	0.0379	0.0321	0.0172
2-CN	—	0	0	0	0	—	0	0	0	0
2-NO_2	—	—	—	0	0	—	—	0	0.0713	0.0575
5-NH_2	0.0144	0.0458	0.0466	0.0849	0.1151	0	0.0263	0.0592	0.0424	0.0271
5-OH	0	0.0112	0.0135	0.0561	0.0829	0	0	0.0278	0.0375	0.0196
5-CH_3	0	0.0091	0.0114	0.0529	0.0792	0	0	0.0257	0.0303	0.0195
5-CN	0	0	0	0.0173	0.0423	0	0	0	0.0456	0.0290
5-NO_2	—	0	0	0	0.0019	—	0	0	0.1103	0.0868
6-NH_2	0	0.0252	0.0265	0.0598	0.0872	0	0.0085	0.0375	0.0252	0.0173
6-OH	0	0	0.0028	0.0499	0.0758	0	0	0.0185	0.0358	0.0188
6-CH_3	0	0	0	0.0462	0.0718	0	0	0.0156	0.0288	0.0186
6-CN	0	0	0	0	0.0236	0	0	0	0.0470	0.0260
6-NO_2	0	0	0	0	0	—	0	0	0.0655	0.0461
2,5,7-NH_2	0.1156	0.0823	0.0835	0.0515	0.0854	0	0.0753	0.0778	0.0013	0.0002
2,5,7-OH	0	0.0115	0.0139	0.0391	0.0633	0	0	0.0234	0.0095	0.0045
2,5,7-CH_3	0	0	0	0.0234	0.0438	0	0	0	0.0142	0.0082
2,5,7-CN	0	0	0	0	0	—	0	0	0	0.0007
2,5,7-NO_2	—	0	0	0	0	—	0	0	0	0
2,5,8-NH_2	0.1568	0.1111	0.1123	0.0648	0.1054	0.0528	0.0886	0.0933	0.0015	0.0002
2,5,8-OH	0.0265	0.0358	0.0391	0.0532	0.0813	0	0.0242	0.0456	0.0078	0.0051
2,5,8-CH_3	0	0.0006	0.0027	0.0319	0.0516	0	0	0.0136	0.0122	0.0065
2,5,8-CN	0	0	0	0	0	—	0	0	0.0126	0.0101
2,5,8-NO_2	—	0	0	0	0	—	0	0	0	0
2,6,8-NH_2	0.1707	0.1239	0.1252	0.0707	0.1013	0.0723	0.0908	0.1033	0.0016	0.0002
2,6,8-OH	0.0347	0.0416	0.0451	0.0570	0.0861	0	0.0309	0.0509	0.0113	0.0053
2,6,8-CH_3	0	0	0	0.0263	0.0453	0	0	0.0039	0.0146	0.0085
2,6,8-CN	0	0	0	0	0	—	0	0	0.0017	0.0020
2,6,8-NO_2	—	0	0	0	0	—	0	0	0	0
Anthraquinones										
H	0.1104	0.1167	0.1107	0.1068	0.1390	0	0.0876	0.1071	0.0242	0.0140
1-NH_2	0.2422	0.2902	0.2771	0.2252	0.2821	0.0825	0.2358	0.2568	0.0432	0.0281
1-OH	0.2033	0.2500	0.2360	0.1955	0.2400	0.0543	0.1974	0.2172	0.0406	0.0195
1-CH_3	0	0	0	0.0252	0.0524	0	0	0	0.0540	0.0351
1-CN	0.1085	0.1944	0.1905	0.1952	0.2377	0.0005	0.1625	0.1919	0.0639	0.0407
1-NO_2	—	0.0426	0.0366	0.1750	0.1336	—	0.0418	0.0705	0.2192	0.1826
2-NH_2	0.2502	0.2230	0.2124	0.1648	0.2099	0.0752	0.1787	0.1871	0.0264	0.0140
2-OH	0.1854	0.2199	0.2059	0.1730	0.2157	0.0418	0.1743	0.1935	0.0323	0.0186
2-CH_3	0.2056	0.2644	0.2549	0.2400	0.2882	0.0495	0.2242	0.2499	0.0740	0.0387
2-CN	0.1006	0.1852	0.1864	0.2431	0.2830	0	0.1724	0.2182	0.1448	0.0861
2-NO_2	0.0368	0.1290	0.1298	0.1285	0.1631	0	0.1086	0.1313	0.0313	0.0150
1,3,5,7-NH_2	0.2052	0.1547	0.1274	0.0582	0.0884	0.1450	0.0936	0.1022	0.0003	0
1,3,5,7-OH	0.1494	0.1206	0.1151	0.0695	0.0978	0.0334	0.0930	0.0929	0.0081	0.0014
1,3,5,7-CH_3	0.1645	0.1410	0.1308	0.0981	0.1370	0.0304	0.1080	0.1201	0.0122	0.0042
1,3,5,7-CN	0	0.0037	0.0058	0.0749	0.0966	0	0	0.0245	0.1076	0.0754
1,3,5,7-NO_2	0	0	0	0	0.0203	—	0	0	0.0966	0.0766

Table 3.12: P (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised NH_2Q	2,5,8-NH_2	2,5,8-OH	2,5,8-CH_3	2,5,8-CN	2,5,8-NO_2	2,6,8-NH_2	2,6,8-OH	2,6,8-CH_3	2,6,8-CN	2,6,8-NO_2
Reduced quinone										
Benzoquinones										
H	0	0	0	0	0.0146	0	0	0	0	0.0193
2-NH_2	—	—	—	—	—	—	—	—	—	—
2-OH	0	0	0	0.0276	0.0362	0	0	0	0.0284	0.0403
2-CH_3	—	—	—	—	—	—	—	—	—	—
2-CN	—	—	—	—	—	—	—	—	—	—
2-NO_2	—	—	—	—	—	—	—	—	—	—
2,5-NH_2	—	—	—	—	—	—	—	—	—	—
2,5-OH	—	—	—	—	—	—	—	—	—	—
2,5-CH_3	—	—	—	—	—	—	—	—	—	—
2,5-CN	—	—	—	0	0	—	—	—	0	0.0027
2,5-NO_2	—	—	—	0	0	—	—	—	0	0
Naphthoquinones										
H	0	0	0	0.0175	0.0210	0	0	0	0.0203	0.0191
2-NH_2	0	0.0633	0.1039	0.0409	0.0343	0	0.0512	0.1126	0.0431	0.0301
2-OH	0	0.0025	0.0558	0.0557	0.0566	0	0	0.0694	0.0595	0.0489
2-CH_3	0	0	0.0208	0.0295	0.0270	0	0	0.0329	0.0318	0.0288
2-CN	—	0	0	0	0.0209	—	0	0	0	0.0332
2-NO_2	—	—	0	0.0570	0.1065	—	0	0	0.0695	0.1132
5-NH_2	0	0	0.0420	0.0461	0.0446	0	0	0.0546	0.0420	0.0370
5-OH	0	0	0.0096	0.0343	0.0317	0	0	0.0231	0.0370	0.0278
5-CH_3	0	0	0.0078	0.0277	0.0259	0	0	0.0210	0.0299	0.0277
5-CN	—	0	0	0.0405	0.0485	0	0	0	0.0449	0.0447
5-NO_2	—	0	0	0.0948	0.1460	—	0	0	0.1083	0.1531
6-NH_2	0	0	0.0220	0.0232	0.0272	0	0	0.0336	0.0250	0.0241
6-OH	0	0	0	0.0326	0.0307	0	0	0.0134	0.0354	0.0329
6-CH_3	0	0	0	0.0322	0.0304	0	0	0.0104	0.0285	0.0267
6-CN	—	0	0	0.0412	0.0450	0	0	0	0.0463	0.0491
6-NO_2	—	0	0	0.0598	0.0871	—	0	0	0.0643	0.0874
2,5,7-NH_2	0	0.0667	0.0820	0.0012	0.0002	0	0.0468	0.0689	0.0013	0.0002
2,5,7-OH	0	0	0.0106	0.0087	0.0090	0	0	0.0188	0.0094	0.0097
2,5,7-CH_3	0	0	0	0.0128	0.0113	0	0	0	0.0140	0.0121
2,5,7-CN	—	0	0	0	0.0443	—	0	0	0	0.0534
2,5,7-NO_2	—	0	0	0	0.0482	—	0	0	0	0.0588
2,5,8-NH_2	0	0.0933	0.0943	0.0014	0.0002	0	0.0713	0.0913	0.0015	0.0002
2,5,8-OH	0	0	0.0340	0.0101	0.0065	0	0	0.0401	0.0078	0.0069
2,5,8-CH_3	0	0	0	0.0142	0.0121	0	0	0.0102	0.0154	0.0129
2,5,8-CN	—	0	0	0	0.0525	—	0	0	0.0110	0.0602
2,5,8-NO_2	—	0	0	0	0	—	0	0	0	0.0116
2,6,8-NH_2	0.0236	0.1071	0.1053	0.0015	0.0002	0	0.0822	0.1013	0.0016	0.0002
2,6,8-OH	0	0.0066	0.0395	0.0105	0.0067	0	0	0.0452	0.0112	0.0071
2,6,8-CH_3	0	0	0	0.0132	0.0115	0	0	0	0.0144	0.0124
2,6,8-CN	—	0	0	0	0.0457	—	0	0	0	0.0547
2,6,8-NO_2	—	0	0	0	0	—	0	0	0	0
Anthraquinones										
H	0	0.0700	0.1020	0.0274	0.0231	0	0.0566	0.1068	0.0240	0.0179
1-NH_2	0.0161	0.2443	0.2546	0.0506	0.0413	0.0194	0.2152	0.2598	0.0430	0.0335
1-OH	0.0058	0.2025	0.2150	0.0389	0.0306	0.0003	0.1778	0.2201	0.0404	0.0318
1-CH_3	0	0	0	0.0481	0.0572	0	0	0	0.0532	0.0619
1-CN	0	0.1342	0.1794	0.0714	0.0485	0	0.1239	0.1892	0.0635	0.0507
1-NO_2	—	0.0148	0.0496	0.2193	0.2186	—	0.0335	0.0779	0.2178	0.2288
2-NH_2	0.0128	0.1858	0.1959	0.0254	0.0226	0.0014	0.1588	0.1914	0.0263	0.0168
2-OH	0.0014	0.1743	0.1915	0.0309	0.0217	0	0.1547	0.1895	0.0321	0.0225
2-CH_3	0.0012	0.2101	0.2446	0.0708	0.0549	0	0.1909	0.2492	0.0736	0.0571
2-CN	—	0.1285	0.1930	0.1374	0.1196	0	0.1270	0.2116	0.1438	0.1250
2-NO_2	—	0.0809	0.1236	0.0296	0.0245	—	0.0810	0.1313	0.0311	0.0257
1,3,5,7-NH_2	0.1072	0.1346	0.1118	0.0002	0	0.1032	0.1075	0.1008	0.0003	0
1,3,5,7-OH	0	0.0972	0.0998	0.0077	0.0017	0	0.0776	0.1065	0.0081	0.0017
1,3,5,7-CH_3	0	0.1109	0.1161	0.0117	0.0094	0	0.0926	0.1171	0.0122	0.0052
1,3,5,7-CN	—	0	0.0033	0.0982	0.1122	0	0	0.0187	0.1064	0.1201
1,3,5,7-NO_2	—	0	0	0.0888	0.1203	—	0	0	0.0950	0.1229

Table 3.13: P (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised AH_2Q	H	1-NH_2	1-OH	1-CH_3	1-CN	1-NO_2	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2
Reduced quinone											
Benzoquinones											
H	0	0	0	0	0	0	0	0	0	0	0
2-NH_2	—	—	—	—	—	—	—	—	—	—	—
2-OH	0	0	0	0	0	0	0	0	0	0	0
2-CH_3	—	—	—	—	—	—	—	—	—	—	—
2-CN	—	—	—	—	—	—	—	—	—	—	—
2-NO_2	—	—	—	—	—	—	—	—	—	—	—
2,5-NH_2	—	—	—	—	—	—	—	—	—	—	—
2,5-OH	—	—	—	—	—	—	—	—	—	—	—
2,5-CH_3	—	—	—	—	—	—	—	—	—	—	—
2,5-CN	—	—	—	—	—	—	—	—	—	—	—
2,5-NO_2	—	—	—	—	—	—	—	—	—	—	—
Naphthoquinones											
H	0	0	0	0	0	0	0	0	0	0	0
2-NH_2	0	0	0	0.1584	0	0	0	0	0	0	0
2-OH	0	0	0	0.0742	0	0	0	0	0	0	0
2-CH_3	0	0	0	0.0417	0	0	0	0	0	0	0
2-CN	0	—	—	—	0	—	—	—	—	0	0
2-NO_2	0	—	—	—	—	—	—	—	—	—	—
5-NH_2	0	0	0	0.0493	0	0	0	0	0	0	0
5-OH	0	0	0	0.0283	0	0	0	0	0	0	0
5-CH_3	0	0	0	0.0325	0	0	0	0	0	0	0
5-CN	0	0	0	0	0	—	0	0	0	0	0
5-NO_2	0	—	—	—	—	—	—	—	—	—	—
6-NH_2	0	0	0	0.0534	0	0	0	0	0	0	0
6-OH	0	0	0	0.0203	0	0	0	0	0	0	0
6-CH_3	0	0	0	0.0232	0	0	0	0	0	0	0
6-CN	0	—	0	0	0	—	0	0	0	0	0
6-NO_2	0	—	—	—	0	—	—	—	—	0	0
2,5,7-NH_2	0.0162	0	0	0.2026	0	0.0146	0	0	0	0.0025	0.0176
2,5,7-OH	0	0	0	0.0606	0	0	0	0	0	0	0
2,5,7-CH_3	0	0	0	0.0226	0	0	0	0	0	0	0
2,5,7-CN	0	—	—	—	0	—	—	—	—	0	0
2,5,7-NO_2	0	—	—	—	0	—	—	—	—	0	—
2,5,8-NH_2	0.0362	0	0	0.2497	0.0340	0.0773	0	0	0	0.0368	0.0577
2,5,8-OH	0	0	0	0.1015	0	0	0	0	0	0	0
2,5,8-CH_3	0	0	0	0.0447	0	0	0	0	0	0	0
2,5,8-CN	0	—	—	—	0	—	—	—	—	0	0
2,5,8-NO_2	0	—	—	—	0	—	—	—	—	0	—
2,6,8-NH_2	0.0452	0	0	0.2677	0.0438	0.1014	0	0.0188	0.0198	0.0463	0.0701
2,6,8-OH	0	0	0	0.1107	0	0	0	0	0	0	0
2,6,8-CH_3	0	0	0	0.0286	0	0	0	0	0	0	0
2,6,8-CN	0	—	—	—	0	—	—	—	—	0	0
2,6,8-NO_2	0	—	—	—	0	—	—	—	—	0	—
Anthraquinones											
H	0	0	0	0.1506	0	0	0	0	0	0	0
1-NH_2	0.1638	0	0.0178	0.2183	0.1171	0.0283	0.0185	0.0396	0.0405	0.1238	0.1243
1-OH	0.1288	0	0	0.1789	0.0832	0.0142	0	0.0138	0.0152	0.0879	0.0946
1-CH_3	0	—	0	0	0	—	—	0	0	0	0
1-CN	0.0552	0	0	0.0794	0	—	0	0	0	0.0043	0.0164
1-NO_2	0.0199	—	—	—	—	—	—	—	—	—	—
2-NH_2	0.1141	0	0.0009	0.2507	0.0749	0.0355	0	0.0194	0.0213	0.0813	0.1093
2-OH	0.1033	0	0	0.1701	0.0600	0.0125	0	0	0.0015	0.0645	0.0765
2-CH_3	0.1248	0	0	0.1993	0.0683	0.0195	0	0	0	0.0737	0.0805
2-CN	0.0515	0	0	0.0724	0	—	0	0	0	0	0.0125
2-NO_2	0.0246	—	—	—	0	—	—	0	0	0	0
1,3,5,7-NH_2	0.0854	0.0916	0.1056	0.3261	0.0842	0.1940	0.1098	0.1066	0.1004	0.0862	0.1176
1,3,5,7-OH	0.0466	0	0	0.2427	0.0207	0.0536	0	0	0	0.0249	0.0434
1,3,5,7-CH_3	0.0503	0	0	0.2568	0.0201	0.0472	0	0	0	0.0245	0.0437
1,3,5,7-CN	0	—	0	0.0052	0	—	0	0	0	0	0
1,3,5,7-NO_2	0	—	—	—	0	—	—	—	—	0	0

Table 3.14: P (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	1,3,5,7-NH_2	1,3,5,7-OH	1,3,5,7-CH_3	1,3,5,7-CN	1,3,5,7-NO_2
Reduced quinone					
Benzoquinones					
H	0	0	0	0	0
2-NH_2	—	—	—	—	—
2-OH	0	0	0	0	0
2-CH_3	—	—	—	—	—
2-CN	—	—	—	—	—
2-NO_2	—	—	—	—	—
2,5-NH_2	—	—	—	—	—
2,5-OH	—	—	—	—	—
2,5-CH_3	—	—	—	—	—
2,5-CN	—	—	—	—	—
2,5-NO_2	—	—	—	—	0
Naphthoquinones					
H	0	0	0	0	0
2-NH_2	0	0	0	0.0200	0.0326
2-OH	0	0	0	0.0159	0.0336
2-CH_3	0	0	0	0.0041	0.0161
2-CN	—	0	0	0	0
2-NO_2	—	—	—	0	0
5-NH_2	0	0	0	0.0108	0.0264
5-OH	0	0	0	0.0016	0.0160
5-CH_3	0	0	0	0.0010	0.0135
5-CN	—	0	0	0	0.0063
5-NO_2	—	—	—	0	0
6-NH_2	0	0	0	0.0038	0.0140
6-OH	0	0	0	0	0.0138
6-CH_3	0	0	0	0	0.0132
6-CN	—	0	0	0	0.0002
6-NO_2	—	0	0	0	0
2,5,7-NH_2	0	0	0	0.0068	0.0068
2,5,7-OH	0	0	0	0.0014	0.0065
2,5,7-CH_3	0	0	0	0	0.0045
2,5,7-CN	—	0	0	0	0
2,5,7-NO_2	—	—	—	0	0
2,5,8-NH_2	0	0.0161	0.0210	0.0066	0.0056
2,5,8-OH	0	0	0	0.0047	0.0094
2,5,8-CH_3	0	0	0	0	0.0053
2,5,8-CN	—	0	0	0	0
2,5,8-NO_2	—	0	0	0	0
2,6,8-NH_2	0	0.0348	0.0381	0.0074	0.0061
2,6,8-OH	0	0	0	0.0055	0.0101
2,6,8-CH_3	0	0	0	0	0.0050
2,6,8-CN	—	0	0	0	0
2,6,8-NO_2	—	0	0	0	0
Anthraquinones					
H	0	0	0	0.0158	0.0191
1-NH_2	0	0.0858	0.0946	0.0464	0.0465
1-OH	0	0.0469	0.0550	0.0337	0.0425
1-CH_3	—	0	0	0	0.0116
1-CN	0	0	0	0.0434	0.0604
1-NO_2	—	—	—	0.1127	0.1546
2-NH_2	0	0.0537	0.0596	0.0264	0.0273
2-OH	0	0.0281	0.0360	0.0309	0.0309
2-CH_3	0	0.0289	0.0367	0.0595	0.0657
2-CN	—	0	0	0.0840	0.1104
2-NO_2	—	0	0	0.0192	0.0279
1,3,5,7-NH_2	0	0.0984	0.0966	0.0037	0.0044
1,3,5,7-OH	0	0	0.0054	0.0083	0.0079
1,3,5,7-CH_3	0	0	0	0.0109	0.0145
1,3,5,7-CN	—	0	0	0	0.0382
1,3,5,7-NO_2	—	0	0	0	0

The following quinone pairs have the highest photorecharging efficiency, P, as defined in Equation 3.1, with the unsubstituted system data provided for reference:

Chemical species		Shockley-Queisser efficiency				Photorechargeability index (eV)
Reduced	Oxidised	ΔE_1 (eV)	ΔE_2 (eV)	f_{SQ}	ΔE_{stored} (eV)	P
AQ	BH_2Q	2.48	2.18	0.13	1.26	0.17
1-NO_2AQ	BH_2Q	1.51	0.994	0.306	1.39	0.425
2-CNAQ	2-CNNH_2Q	1.77	1.52	0.276	1.53	0.422
1-NO_2AQ	2-CNBH_2Q	1.84	1.85	0.267	1.50	0.401
1-NH_2AQ	5-NO_2NH_2Q	1.62	0.93	0.297	1.31	0.391
1-NO_2AQ	2-NO_2BH_2Q	1.98	1.99	0.234	1.63	0.380
2-CNAQ	BH_2Q	2.17	1.73	0.267	1.42	0.378
1-NH_2AQ	2-NH_2BH_2Q	1.75	1.77	0.276	1.34	0.371
1-NO_2AQ	2-CNNH_2Q	1.45	0.80	0.243	1.49	0.363
2-CH_3AQ	2-CNNH_2Q	2.12	1.77	0.205	1.77	0.361

Table 3.15: Pairs of quinone which have the highest photo-recharging efficiency, with unsubstituted anthraquinone and benzohydroquinone as a reference. ΔE_1, ΔE_2 and ΔE_{stored} are as defined in Figure 3.1. f_{SQ} is the Shockley-Queisser efficiency of the least efficient step of ΔE_1 and ΔE_2

1-NO_2AQ and BH_2Q has the highest photorechargeability index of 0.425 eV and stores 1.39 eV. However, the cell of 2-CNAQ and 2-CNNH_2Q stores more energy (1.53 eV) for a modest decrease in photorechargeability index (0.422). These two cells appear to be the best candidates for developing an all-quinone photorechargeable battery. By tuning the ring system size and substituting with functional groups, significant gains can be made in both the ΔE_{stored} and photorechargeability of quinone battery when compared to unsubstituted anthraquinone and benzohydroquinone.

The photorechargeability index of each combination of quinone and anthraquinone was determined. The distribution of these 1,653 indices is given in Table 3.16.

P (eV)	Number of redox pairs
0–0.05	690
0.05–0.10	334
0.1–0.15	212
0.15–0.20	117
0.2–0.25	104
0.25–0.30	40
0.3–0.35	17
0.35–0.40	6
0.4–0.45	3

Table 3.16: Ranges of the photorechargeability index, P, and how many of the 1,653 cells achieve each range

Cells which have the highest photorechargeability index generally comprise an anthraquinone and a benzohydroquinone or naphthohydroquinone, where both the oxidised species and reduced species are singly-substituted.

3.4 Conclusions

The energy stored by an all-quinone battery can be manipulated by tuning ring system size and functional group substitution. Extending the size of the ring system increases the values of ΔE_1, ΔE_2 and ΔE_{stored} for reduction, but decreases them for oxidation. Substitution with electron-donating groups raises the ΔE values for reduction and lowers the values for oxidation, while electron-withdrawing groups have the opposite effect. Of the cells studied, the one which stores the most energy is cell of 1,3,5,7-NH_2A as the catholyte and 2,5-NO_2BH_2 as the anolyte, which can store 2.68 eV, more than a lead-acid cell. Photorechargeability of an all-quinone battery can also be achieved by tuning ring conjugation and functional group substitution, so that energy barriers can be overcome by solar radiation. This is harder to predict because the competing desires to maximise ΔE_{stored} while optimising barrier heights mean a balance between the two is required. Cells comprising 1-NO_2A as the catholyte and BH_2 as the anolyte or 2-CNAQ and 2-$CNNH_2$Q as the catholyte and anolyte respectively store 1.4–1.5 eV and have high photorechargeability indices.

Chapter 4

Redox-active organic radicals

4.1 Introduction

The previous chapter explored the two-election, two-proton redox reactions of quinones in pursuit of a photorechargeable battery. The major advantage of transferring protons after each redox step is that they neutralise the charged intermediates and products, improving overall stability. In particular, both sets of products, the reduced (hydroquinone) and oxidised (quinone) forms, are long-term shelf-stable in a dry environment. However, during the exothermic proton transfer step a significant fraction of the energy used to overcome the charging barriers is lost and the reaction becomes kinetically rate-limited by proton-transfer processes. To overcome this deficit, this chapter studies one-electron transfers to and from persistent radical species.

Radical chemical species contain electrons which are not spin-paired, so are generally unstable. Radical stability can be increased through kinetic protection using bulky groups to raise the activation energy of decomposition. This allows for the existence of radicals are stable enough to be observed spectroscopically, and some that can be isolated, characterised and even stored. For example, the first organic radical to be characterised was the triphenylmethyl radical, which is a trivalent carbon atom sterically protected by three phenyl groups.[53] More recently, the redox chemistry of organic radicals has been studied. Previous research has shown an organic RFB comprising MV and 4-hydroxy-TEMPO to be promising, with a cell voltage of 1.25 V and capacity for 100 cycles at very high Coulombic efficiency.[29]

The aim of this chapter is to calculate the one-electron redox potentials for a range of radical molecules identified as stable in the chemical literature, as the first step towards establishing redox pairs of organic radical species for use in RFBs. Redox pairs with the highest calculated redox potential differences will give the highest energy stored. Additionally, redox pairs which have redox potential difference of 0.8–2.0 V (store 0.8–2.0 eV of energy) are suitable candidates for use in a photorechargeable RFB, as their charging energies lie in the region with the highest Shockley-Queisser efficiency limits.

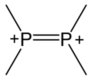
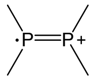
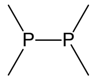
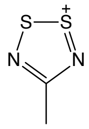
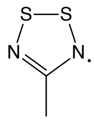
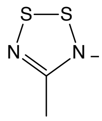
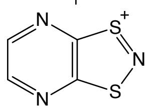
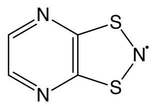
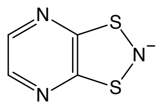
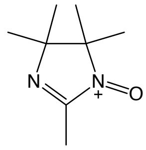
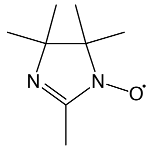
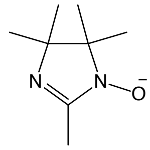
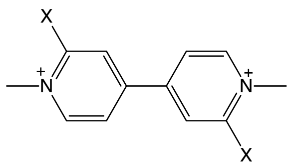
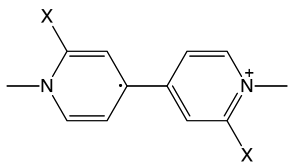
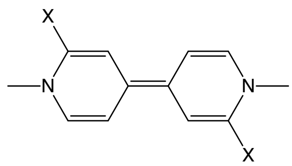
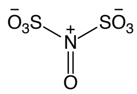
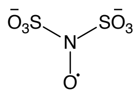
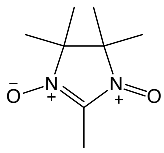
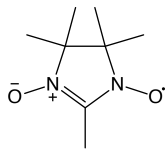
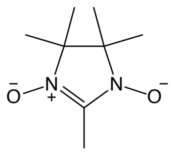
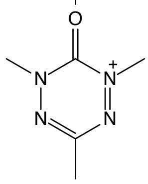
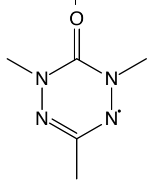
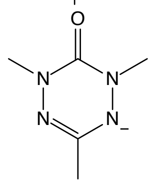
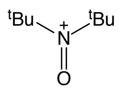
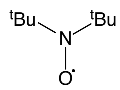
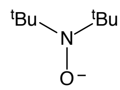
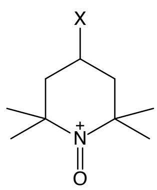
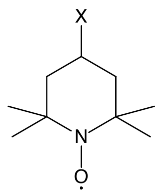
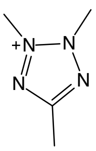
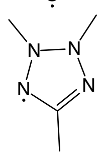
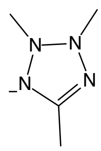
4.2 Methods

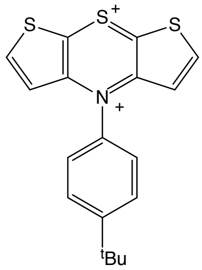
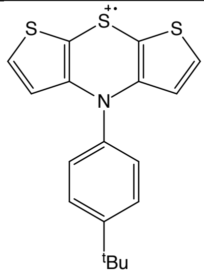
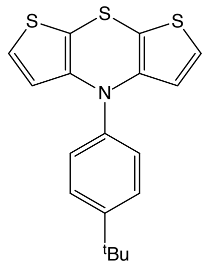
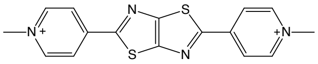
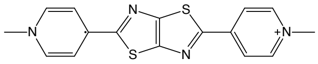
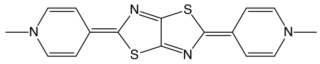
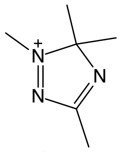
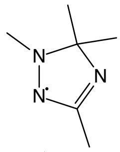
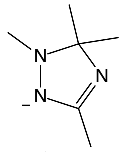
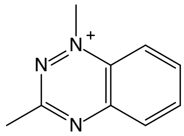
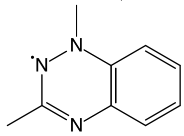
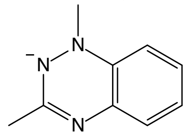
The reduction and oxidation reaction energies were computed for the radical species in Figure 4.1, inspired by known persistent and stable radical species.[25,29,54,55] All calculations were performed using the Q-Chem 4 quantum chemistry program package.[34] Radical species geometries were optimised at B3LYP[35,36]/6-311G(d).[37,52] Vertical electron transfer was modelled; all single-point energy calculations used the radical optimised geometries. Single-point energy calculations were performed at B3LYP/6-311+G(2d,p).[37,42,44,52] Solvation effects were approximated with the C-PCM model[39–41] with a dielectric constant of 10. Vibrational energies and entropic corrections were not accounted for. It has been determined in Chapter 2 that $\Delta H \approx \Delta G$ is valid within the margins of error of the methods to calculate ΔH and ΔG_{solv} (DFT and C-PCM, respectively).

Table 4.1: Molecules for which the one-electron oxidation and reduction potentials were calculated.

$\Delta H_1 = \mathrm{H_{ox}}$ - $\mathrm{H_{rad}}$ and $\Delta E°_1 = \mathrm{nFH_1}$ - $\mathrm{E°_{SHE}}$

$\Delta H_2 = \mathrm{H_{rad}}$ - $\mathrm{H_{red}}$ and $\Delta E°_2 = \mathrm{nFH_2}$ - $\mathrm{E°_{SHE}}$

Name	Oxidised	Radical	Reduced	Ref.
Diphosphine				56
Dithiadiazolyl				25
Dithiazolyl				25
Iminonitroxide				25
Methyl viologen (MV) (X = H, CH_3, CN, NH_2, NO_2, OH)				29
Nitrosodisulfonate				25
Nitronyl nitroxide				25
Oxoverdazyl				25
t-Butyl nitroxide				25
TEMPO (X = H, COOH, NH_2, O, OCH_3, OH)				29
Tetrazolinyl				25

Name	Oxidised	Radical	Reduced	Ref.
Thiazine				55
Thiazolothiazole				54
Triazolyl				25
Triazinyl				25

Trivalent nitrogen-containing heterocycles and aminoxyl radicals make up most of these species. Exceptions are the diphosphine radical, which has an unpaired electron shared between the phosphorus atoms, and the methyl viologens, in which the radical is formally located on a carbon atom. Unsubstituted and 4,4'-disubstituted methyl viologens were studied, with methyl, cyano, amino, nitro and hydroxyl groups acting as substitutents. TEMPO was substituted in the 4-position with carboxyl, amino, carbonyl methoxy and hydroxy groups. For all molecules except nitrosodisulfonate and the TEMPO and MV derivatives, the energy of both reduction and oxidation from the radical was calculated. The reduced form of nitrosodisulfonate is a trianion which is unlikely to be persistent. The MV and thiazine dications are known to exist.[29,55] Viologens are most well-known in their dicationic form and strong chemical reductants are required to convert it to the neutral form,[57] so only the redox between the dication and radical cation was studied here. Similarly, TEMPO and its derivatives are widely studied for their oxidation to their cations, rather than reduction to their anions.[29] Results are reported as reduction potentials, as is convention, with the first reduction potential to give the radical ($E^{\circ}{}_1$) and the second reduction potential that of transferring an electron to the radical ($E^{\circ}{}_2$). Results are given versus the standard hydrogen electrode (SHE), using the absolute value for the SHE of +4.44 V given by Trasatti.[58] This is shown in Equations 4.1 to 4.4:

$$\Delta H_1 = H_{\mathrm{ox}} - H_{\mathrm{rad}} \tag{4.1}$$

$$\Delta H_1 = H_{\mathrm{rad}} - H_{\mathrm{red}} \tag{4.2}$$

$$E^\circ{}_1 = nFH_1 - \Delta E^\circ{}_{\mathrm{SHE}} \tag{4.3}$$

$$E^\circ{}_2 = nFH_2 - \Delta E^\circ{}_{\mathrm{SHE}} \tag{4.4}$$

where H_{ox}, H_{rad} and H_{red} are the calculated enthalpies of the oxidised, radical and reduced species, respectively; n is the number of electrons transferred (1 in this work); F is the Faraday constant; and $E^\circ{}_{\mathrm{SHE}}$ is the absolute potential of the SHE.

4.3 Results and discussion

The calculated reduction potentials of each species are given in Table 4.2.

Table 4.2: Calculated standard reduction potentials versus the SHE

Name	$E^\circ{}_1$ (V)	$E^\circ{}_2$ (V)
Diphosphine	+2.32	+0.96
Thiazoles		
Dithiadiazolyl	+0.71	-0.79
Dithiazolyl	+0.15	-0.50
Thiazine	+1.88	+0.31
Thiazolothiazole	-0.58	-0.18
Aminoxyls		
Iminonitroxide	+1.28	-1.40
Nitronyl nitroxide	+0.61	
Nitrosodisulfonate	-1.39	
tBu-nitroxide	+0.78	-2.41
N-containing heterocycles		
Oxoverdazyl	+0.86	-1.83
Tetrazolinyl	+0.33	-2.33
Triazinyl	+0.05	-1.42
Triazolyl	-0.01	-1.37
TEMPO derivatives		
4-O TEMPO	+1.07	
4-COOH TEMPO	+0.93	
4-OH TEMPO	+0.91	
4-OCH_3 TEMPO	+0.91	
4-NH_2 TEMPO	+0.86	
TEMPO	+0.80	
Methyl viologens		
NO_2-MV	+1.27	
CN-MV	+1.11	
H-MV	+0.42	
OH-MV	+0.29	
CH_3-MV	+0.25	
NH_2-MV	-0.12	

The second reduction potential is generally more negative than the first, as the electron is being added to a more electron-rich molecule for the second reduction. Diphosphine has two of the most positive reduction potentials, as it is favourable to reduce a small dication and then radical cation to a small neutral singlet species. Of the thiazoles, the thiazine has the most positive $E°_1$, as this reduction converts a dication to a radical cation. The decrease in positive charge and the large system over which the radical can delocalise makes this reduction favourable. The value of $E°_2$ for dithiadiazolyl is the most negative due to the small ring system and lack of electron-withdrawing groups, making the addition of an electron an unfavourable process. Regarding aminoxyls, both the iminonitroxide and *t*-butyl nitroxide both have moderately high positive $E°_1$ values, but quite negative values for $E°_2$ due to the negative charge concentrated on the small nitrogen atom in the anionic reduced forms. The $E°_1$ values for the N-containing heterocycles are all mildly positive, due to the conjugation in the rings allowing for effective delocalisation of the positive charge and unpaired electron. The reduction potential of substituted TEMPO is greater than for unsubstituted TEMPO. This effect is true for both electron-donating and electron-withdrawing substitutions, but is more pronounced for the electron-withdrawing susbtitutions (carbonyl and carboxylic acid groups). The TEMPO framework is not conjugated, so the effects of substitution on reduction potentials are likely due to ring strain rather than through-bond effects. The aromatic nature of MV means that disubstituting with electron-withdrawing and -donating groups predictably increases and decreases the energies of reduction, respectively. This results in the order of reduction potentials with the most electron-poor viologen (NO_2-MV) having the most positive reduction potential down to the most electron-rich viologen (NH_2-MV) having the most negative reduction potential. For analysing the best oxidants and reductants it is helpful to view the results in order of reduction potential, as in Table 4.3. These reduction potentials lie over a large range, allowing a maximum cell voltage of 4.7 V for a cell comprising diphosphine dication as the catholyte (+2.3 V) and *t*-butyl nitroxide anion as the anolyte (-2.4 V) when discharging. This is over twice the voltage of lead-acid and lithium-ion batteries (2.1 V and 2.6 V, respectively).[45,51] The electrochemistry of these radical species is not very well studied. Given that methyl viologens have well-known redox behaviour and stability, the combination of CN-MV (+1.11 V) and NH_2-MV (-0.12 V) is a promising pair with established electrochemistry and a cell potential of 1.23 V.

Table 4.3: Calculated standard reduction potentials versus the SHE, ordered from highest to lowest

Name	E° (V)	Name	E° (V)
Diphosphine $E^\circ{}_1$	+2.32	Triazolyl $E^\circ{}_1$	-0.01
Thiazine $E^\circ{}_1$	+1.88	NH_2-MV	-0.12
Iminonitroxide $E^\circ{}_1$	+1.28	Thiazolothiazole $E^\circ{}_2$	-0.18
CN-MV	+1.11	Nitroxide $E^\circ{}_2$	-0.40
4-O TEMPO	+1.07	Dithiazolyl $E^\circ{}_2$	-0.50
Diphosphine $E^\circ{}_2$	+0.96	Thiazolothiazole $E^\circ{}_1$	-0.58
4-COOH TEMPO	+0.93	Dithiadiazolyl $E^\circ{}_2$	-0.79
4-OH TEMPO	+0.91	Triazolyl $E^\circ{}_2$	-1.37
4-OCH_3 TEMPO	+0.91	Nitroxide $E^\circ{}_1$	-1.39
Oxoverdazyl $E^\circ{}_1$	+0.86	Iminonitroxide $E^\circ{}_2$	-1.40
4-NH_2 TEMPO	+0.86	Nitronyl nitroxide $E^\circ{}_2$	-1.42
TEMPO	+0.80	Triazinyl $E^\circ{}_2$	-1.42
t-Bu-nitroxide $E^\circ{}_1$	+0.78	Oxoverdazyl $E^\circ{}_2$	-1.83
Dithiadiazolyl $E^\circ{}_1$	+0.71	Tetrazolinyl $E^\circ{}_2$	-2.33
Nitronyl nitroxide $E^\circ{}_1$	+0.61	t-Bu-nitroxide $E^\circ{}_2$	-2.41
MV	+0.42		
Tetrazolinyl $E^\circ{}_1$	+0.33		
Thiazine $E^\circ{}_2$	+0.31		
NO_2-MV	+0.29		
CH_3-MV	+0.25		
Dithiazolyl $E^\circ{}_1$	+0.15		
Triazinyl $E^\circ{}_1$	+0.05		

For each cell (combination of two redox couples) the cell potential, $E^\circ{}_{\text{cell}}$, can be determined (4.5:

$$E^\circ{}_{\text{cell}} = E^\circ{}_{\text{reduction}} - E^\circ{}_{\text{oxidation}} \tag{4.5}$$

Where $E^\circ{}_{\text{reduction}}$ is the reduction potential of the redox couple being reduced and $E^\circ{}_{\text{oxidation}}$ is the reduction potential of the redox couple being oxidised. 666 cells can be composed and the distribution of $E^\circ{}_{\text{cell}}$ is given in Table 4.4. The highest Shockley-Queisser efficiencies are for photons carrying 0.8–2.0 eV of energy. Therefore, organic radical batteries with values of energy stored within this range are suitable candidates for photorecharging. Of the 666 cells studied, 249 store 0.8–2.0 eV of energy. They are listed in Table 4.5.

E°_{cell} (V)	Number of redox pairs
0–0.5	171
0.5–1.0	148
1.0–1.5	107
1.5–2.0	77
2.0–2.5	83
2.5–3.0	37
3.0–3.5	29
3.5–4.0	9
4.0–4.5	3
4.5–5.0	2

Table 4.4: Ranges of E°_{cell} and how many of the 666 cells achieve each range

Table 4.5: Combined cells which store between 0.8 and 2.0 eV

Reduced upon charging	Oxidised upon charging	E_{stored} (eV)
Nitroxide $E°_1$	Nitronyl nitroxide $E°_1$	2.00
Tetrazolinyl $E°_1$	Diphosphine $E°_1$	1.99
Oxoverdazyl $E°_2$	Dithiazolyl $E°_1$	1.98
Triazolyl $E°_2$	Nitronyl nitroxide $E°_1$	1.98
Tetrazolinyl $E°_2$	Nitroxide $E°_2$	1.94
tBu-nitroxide $E°_2$	Dithiazolyl $E°_2$	1.90
MV	Diphosphine $E°_1$	1.90
Dithiadiazolyl $E°_2$	CN-MV	1.90
Triazolyl $E°_1$	Thiazine $E°_1$	1.89
Oxoverdazyl $E°_2$	Triazinyl $E°_1$	1.88
Thiazolothiazole $E°_1$	Iminonitroxide $E°_1$	1.87
Dithiadiazolyl $E°_2$	4-O TEMPO	1.86
Triazinyl $E°_2$	MV	1.84
Nitronyl nitroxide $E°_2$	MV	1.84
Triazinyl $E°_1$	Thiazine $E°_1$	1.84
Tetrazolinyl $E°_2$	Dithiazolyl $E°_2$	1.83
Oxoverdazyl $E°_2$	Triazolyl $E°_1$	1.82
tBu-nitroxide $E°_2$	Thiazolothiazole $E°_1$	1.82
Iminonitroxide $E°_2$	MV	1.82
Nitroxide $E°_1$	MV	1.81
Triazolyl $E°_2$	MV	1.79
Dithiazolyl $E°_2$	Iminonitroxide $E°_1$	1.78
Triazinyl $E°_2$	Tetrazolinyl $E°_1$	1.75
Nitronyl nitroxide $E°_2$	Tetrazolinyl $E°_1$	1.75
Tetrazolinyl $E°_2$	Thiazolothiazole $E°_1$	1.75
Dithiadiazolyl $E°_2$	Diphosphine $E°_2$	1.75
Dithiazolyl $E°_1$	Thiazine $E°_1$	1.73
Iminonitroxide $E°_2$	Tetrazolinyl $E°_1$	1.73
Triazinyl $E°_2$	Thiazine $E°_2$	1.73
Nitronyl nitroxide $E°_2$	Thiazine $E°_2$	1.72
Nitroxide $E°_1$	Tetrazolinyl $E°_1$	1.72
Nitronyl nitroxide $E°_1$	Diphosphine $E°_1$	1.72
Oxoverdazyl $E°_2$	NH2-MV	1.71
Dithiadiazolyl $E°_2$	4-COOH TEMPO	1.71
Triazinyl $E°_2$	NO2-MV	1.71
Nitronyl nitroxide $E°_2$	NO2-MV	1.71
Iminonitroxide $E°_2$	Thiazine $E°_2$	1.70
Triazolyl $E°_2$	Tetrazolinyl $E°_1$	1.70
Dithiadiazolyl $E°_2$	4-OH TEMPO	1.70
Nitroxide $E°_1$	Thiazine $E°_2$	1.70
Thiazolothiazole $E°_1$	CN-MV	1.69
Dithiadiazolyl $E°_2$	4-OCH3 TEMPO	1.69
Iminonitroxide $E°_2$	NO2-MV	1.69
Nitroxide $E°_1$	NO2-MV	1.68
Nitroxide $E°_2$	Iminonitroxide $E°_1$	1.68
Triazolyl $E°_2$	Thiazine $E°_2$	1.68
Triazinyl $E°_2$	CH3-MV	1.67
Nitronyl nitroxide $E°_2$	CH3-MV	1.67
Triazolyl $E°_2$	NO2-MV	1.66
Thiazolothiazole $E°_1$	4-O TEMPO	1.66
Oxoverdazyl $E°_2$	Thiazolothiazole $E°_2$	1.66
Iminonitroxide $E°_2$	CH3-MV	1.65
Dithiadiazolyl $E°_2$	Oxoverdazyl $E°_1$	1.65
Dithiadiazolyl $E°_2$	4-NH2 TEMPO	1.64
Nitroxide $E°_1$	CH3-MV	1.64
CH3-MV	Thiazine $E°_1$	1.63
tBu-nitroxide $E°_2$	Dithiadiazolyl $E°_2$	1.62

Reduced	Oxidised	E_{stored} (eV)
Triazolyl $E°_2$	CH3-MV	1.62
Dithiazolyl $E°_2$	CN-MV	1.61
Dithiadiazolyl $E°_1$	Diphosphine $E°_1$	1.61
NO2-MV	Thiazine $E°_1$	1.59
Dithiadiazolyl $E°_2$	TEMPO	1.59
Thiazine $E°_2$	Thiazine $E°_1$	1.58
Dithiazolyl $E°_2$	4-O TEMPO	1.57
Triazinyl $E°_2$	Dithiazolyl $E°_1$	1.57
Nitronyl nitroxide $E°_2$	Dithiazolyl $E°_1$	1.57
Dithiadiazolyl $E°_2$	tBu-nitroxide $E°_1$	1.57
Tetrazolinyl $E°_1$	Thiazine $E°_1$	1.55
Tetrazolinyl $E°_2$	Dithiadiazolyl $E°_2$	1.55
Iminonitroxide $E°_2$	Dithiazolyl $E°_1$	1.55
Thiazolothiazole $E°_1$	Diphosphine $E°_2$	1.55
tBu-nitroxide $E°_1$	Diphosphine $E°_1$	1.54
Nitroxide $E°_1$	Dithiazolyl $E°_1$	1.54
TEMPO	Diphosphine $E°_1$	1.52
Triazolyl $E°_2$	Dithiazolyl $E°_1$	1.52
Thiazolothiazole $E°_1$	4-COOH TEMPO	1.51
Nitroxide $E°_2$	CN-MV	1.51
Dithiadiazolyl $E°_2$	Dithiadiazolyl $E°_1$	1.50
Thiazolothiazole $E°_1$	4-OH TEMPO	1.50
Thiazolothiazole $E°_1$	4-OCH3 TEMPO	1.49
Nitroxide $E°_2$	4-O TEMPO	1.47
Triazinyl $E°_2$	Triazinyl $E°_1$	1.47
4-NH2 TEMPO	Diphosphine $E°_1$	1.47
Nitronyl nitroxide $E°_2$	Triazinyl $E°_1$	1.46
Oxoverdazyl $E°_1$	Diphosphine $E°_1$	1.46
Dithiazolyl $E°_2$	Diphosphine $E°_2$	1.46
MV	Thiazine $E°_1$	1.46
Thiazolothiazole $E°_2$	Iminonitroxide $E°_1$	1.46
Thiazolothiazole $E°_1$	Oxoverdazyl $E°_1$	1.45
Iminonitroxide $E°_2$	Triazinyl $E°_1$	1.44
Thiazolothiazole $E°_1$	4-NH2 TEMPO	1.44
Oxoverdazyl $E°_2$	Nitroxide $E°_2$	1.44
Nitroxide $E°_1$	Triazinyl $E°_1$	1.44
Dithiazolyl $E°_2$	4-COOH TEMPO	1.43
4-OCH3 TEMPO	Diphosphine $E°_1$	1.42
Triazolyl $E°_2$	Triazinyl $E°_1$	1.42
Dithiazolyl $E°_2$	4-OH TEMPO	1.41
4-OH TEMPO	Diphosphine $E°_1$	1.41
Triazinyl $E°_2$	Triazolyl $E°_1$	1.41
Dithiazolyl $E°_2$	4-OCH3 TEMPO	1.41
Nitronyl nitroxide $E°_2$	Triazolyl $E°_1$	1.41
NH2-MV	Iminonitroxide $E°_1$	1.40
4-COOH TEMPO	Diphosphine $E°_1$	1.40
Dithiadiazolyl $E°_2$	Nitronyl nitroxide $E°_1$	1.39
Thiazolothiazole $E°_1$	TEMPO	1.39
Iminonitroxide $E°_2$	Triazolyl $E°_1$	1.39
Nitroxide $E°_1$	Triazolyl $E°_1$	1.38
Thiazolothiazole $E°_1$	tBu-nitroxide $E°_1$	1.36
Diphosphine $E°_2$	Diphosphine $E°_1$	1.36
Dithiazolyl $E°_2$	Oxoverdazyl $E°_1$	1.36
Dithiazolyl $E°_2$	4-NH2 TEMPO	1.36
Triazolyl $E°_2$	Triazolyl $E°_1$	1.36
Nitroxide $E°_2$	Diphosphine $E°_2$	1.36
Oxoverdazyl $E°_2$	Dithiazolyl $E°_2$	1.33
Nitroxide $E°_2$	4-COOH TEMPO	1.32
Nitroxide $E°_2$	4-OH TEMPO	1.31
Dithiazolyl $E°_2$	TEMPO	1.30
Nitroxide $E°_2$	4-OCH3 TEMPO	1.30
Triazinyl $E°_2$	NH2-MV	1.30

Reduced	Oxidised	E_{stored} (eV)
Thiazolothiazole $E°_1$	Dithiadiazolyl $E°_1$	1.30
Nitronyl nitroxide $E°_2$	NH2-MV	1.30
Triazolyl $E°_1$	Iminonitroxide $E°_1$	1.29
Thiazolothiazole $E°_2$	CN-MV	1.29
Dithiazolyl $E°_2$	tBu-nitroxide $E°_1$	1.28
Iminonitroxide $E°_2$	NH2-MV	1.28
Nitronyl nitroxide $E°_1$	Thiazine $E°_1$	1.27
Nitroxide $E°_1$	NH2-MV	1.27
Nitroxide $E°_2$	Oxoverdazyl $E°_1$	1.26
Nitroxide $E°_2$	4-NH2 TEMPO	1.25
Thiazolothiazole $E°_2$	4-O TEMPO	1.25
Triazolyl $E°_2$	NH2-MV	1.25
4-O TEMPO	Diphosphine $E°_1$	1.25
Oxoverdazyl $E°_2$	Thiazolothiazole $E°_1$	1.25
Triazinyl $E°_2$	Thiazolothiazole $E°_2$	1.24
Nitronyl nitroxide $E°_2$	Thiazolothiazole $E°_2$	1.24
Triazinyl $E°_1$	Iminonitroxide $E°_1$	1.23
NH2-MV	CN-MV	1.23
Iminonitroxide $E°_2$	Thiazolothiazole $E°_2$	1.22
Dithiazolyl $E°_2$	Dithiadiazolyl $E°_1$	1.22
Nitroxide $E°_1$	Thiazolothiazole $E°_2$	1.21
CN-MV	Diphosphine $E°_1$	1.21
Dithiadiazolyl $E°_2$	MV	1.21
Nitroxide $E°_2$	TEMPO	1.20
NH2-MV	4-O TEMPO	1.19
Thiazolothiazole $E°_1$	Nitronyl nitroxide $E°_1$	1.19
Triazolyl $E°_2$	Thiazolothiazole $E°_2$	1.19
Nitroxide $E°_2$	tBu-nitroxide $E°_1$	1.18
Dithiadiazolyl $E°_1$	Thiazine $E°_1$	1.17
Thiazolothiazole $E°_2$	Diphosphine $E°_2$	1.14
Dithiazolyl $E°_1$	Iminonitroxide $E°_1$	1.13
Triazolyl $E°_1$	CN-MV	1.12
Dithiadiazolyl $E°_2$	Tetrazolinyl $E°_1$	1.12
Nitroxide $E°_2$	Dithiadiazolyl $E°_1$	1.11
Dithiazolyl $E°_2$	Nitronyl nitroxide $E°_1$	1.11
Thiazolothiazole $E°_2$	4-COOH TEMPO	1.11
tBu-nitroxide $E°_1$	Thiazine $E°_1$	1.10
Dithiadiazolyl $E°_2$	Thiazine $E°_2$	1.09
Thiazolothiazole $E°_2$	4-OH TEMPO	1.09
Triazolyl $E°_1$	4-O TEMPO	1.09
Thiazolothiazole $E°_2$	4-OCH3 TEMPO	1.08
NH2-MV	Diphosphine $E°_2$	1.08
TEMPO	Thiazine $E°_1$	1.08
Dithiadiazolyl $E°_2$	NO2-MV	1.08
Triazinyl $E°_1$	CN-MV	1.06
Oxoverdazyl $E°_2$	Dithiadiazolyl $E°_2$	1.05
NH2-MV	4-COOH TEMPO	1.05
Iminonitroxide $E°_1$	Diphosphine $E°_1$	1.04
Thiazolothiazole $E°_2$	Oxoverdazyl $E°_1$	1.04
tBu-nitroxide $E°_2$	Triazolyl $E°_2$	1.04
Thiazolothiazole $E°_2$	4-NH2 TEMPO	1.04
Dithiadiazolyl $E°_2$	CH3-MV	1.04
NH2-MV	4-OH TEMPO	1.03
CH3-MV	Iminonitroxide $E°_1$	1.03
Triazinyl $E°_1$	4-O TEMPO	1.03
NH2-MV	4-OCH3 TEMPO	1.03
Triazinyl $E°_2$	Nitroxide $E°_2$	1.03
4-NH2 TEMPO	Thiazine $E°_1$	1.02
Nitronyl nitroxide $E°_2$	Nitroxide $E°_2$	1.02
Oxoverdazyl $E°_1$	Thiazine $E°_1$	1.02
tBu-nitroxide $E°_2$	Nitroxide $E°_1$	1.01
tBu-nitroxide $E°_2$	Iminonitroxide $E°_2$	1.01

Reduced	Oxidised	E_{stored} (eV)
Thiazolothiazole $E°_1$	MV	1.00
Nitroxide $E°_2$	Nitronyl nitroxide $E°_1$	1.00
Iminonitroxide $E°_2$	Nitroxide $E°_2$	1.00
Nitroxide $E°_1$	Nitroxide $E°_2$	1.00
NO2-MV	Iminonitroxide $E°_1$	0.99
tBu-nitroxide $E°_2$	Nitronyl nitroxide $E°_2$	0.99
tBu-nitroxide $E°_2$	Triazinyl $E°_2$	0.98
Thiazolothiazole $E°_2$	TEMPO	0.98
NH2-MV	Oxoverdazyl $E°_1$	0.98
NH2-MV	4-NH2 TEMPO	0.98
4-OCH3 TEMPO	Thiazine $E°_1$	0.98
Thiazine $E°_2$	Iminonitroxide $E°_1$	0.97
Triazolyl $E°_2$	Nitroxide $E°_2$	0.97
Triazolyl $E°_1$	Diphosphine $E°_2$	0.97
4-OH TEMPO	Thiazine $E°_1$	0.97
Tetrazolinyl $E°_2$	Triazolyl $E°_2$	0.96
Dithiazolyl $E°_1$	CN-MV	0.96
Thiazolothiazole $E°_2$	tBu-nitroxide $E°_1$	0.96
4-COOH TEMPO	Thiazine $E°_1$	0.95
Tetrazolinyl $E°_1$	Iminonitroxide $E°_1$	0.95
Tetrazolinyl $E°_2$	Nitroxide $E°_1$	0.94
Triazolyl $E°_1$	4-COOH TEMPO	0.94
Tetrazolinyl $E°_2$	Iminonitroxide $E°_2$	0.93
Dithiadiazolyl $E°_2$	Dithiazolyl $E°_1$	0.93
Triazolyl $E°_1$	4-OH TEMPO	0.93
Dithiazolyl $E°_1$	4-O TEMPO	0.92
NH2-MV	TEMPO	0.92
Dithiazolyl $E°_2$	MV	0.92
Diphosphine $E°_2$	Thiazine $E°_1$	0.92
Triazinyl $E°_2$	Dithiazolyl $E°_2$	0.92
Triazolyl $E°_1$	4-OCH3 TEMPO	0.92
Nitronyl nitroxide $E°_2$	Dithiazolyl $E°_2$	0.92
Thiazolothiazole $E°_1$	Tetrazolinyl $E°_1$	0.92
Triazinyl $E°_1$	Diphosphine $E°_2$	0.91
Tetrazolinyl $E°_2$	Nitronyl nitroxide $E°_2$	0.91
Tetrazolinyl $E°_2$	Triazinyl $E°_2$	0.91
NH2-MV	tBu-nitroxide $E°_1$	0.90
Iminonitroxide $E°_2$	Dithiazolyl $E°_2$	0.90
Thiazolothiazole $E°_2$	Dithiadiazolyl $E°_1$	0.89
Thiazolothiazole $E°_1$	Thiazine $E°_2$	0.89
Nitroxide $E°_1$	Dithiazolyl $E°_2$	0.89
Triazinyl $E°_1$	4-COOH TEMPO	0.88
Thiazolothiazole $E°_1$	NO2-MV	0.87
Triazolyl $E°_1$	Oxoverdazyl $E°_1$	0.87
Triazolyl $E°_1$	4-NH2 TEMPO	0.87
Triazolyl $E°_2$	Dithiazolyl $E°_2$	0.87
Triazinyl $E°_1$	4-OH TEMPO	0.87
MV	Iminonitroxide $E°_1$	0.86
Triazinyl $E°_1$	4-OCH3 TEMPO	0.86
CH3-MV	CN-MV	0.86
Triazinyl $E°_2$	Thiazolothiazole $E°_1$	0.84
Thiazolothiazole $E°_1$	CH3-MV	0.83
NH2-MV	Dithiadiazolyl $E°_1$	0.83
Nitronyl nitroxide $E°_2$	Thiazolothiazole $E°_1$	0.83
Dithiazolyl $E°_2$	Tetrazolinyl $E°_1$	0.83
Dithiadiazolyl $E°_2$	Triazinyl $E°_1$	0.83
CH3-MV	4-O TEMPO	0.82
NO2-MV	CN-MV	0.82
Nitroxide $E°_2$	MV	0.82
Triazolyl $E°_1$	TEMPO	0.82
Triazinyl $E°_1$	Oxoverdazyl $E°_1$	0.81
Iminonitroxide $E°_2$	Thiazolothiazole $E°_1$	0.81

Reduced	Oxidised	E_{stored} (eV)
Triazinyl $E°_1$	4-NH2 TEMPO	0.81
Dithiazolyl $E°_1$	Diphosphine $E°_2$	0.81
4-O TEMPO	Thiazine $E°_1$	0.81
Dithiazolyl $E°_2$	Thiazine $E°_2$	0.81
Nitroxide $E°_1$	Thiazolothiazole $E°_1$	0.81
Thiazine $E°_2$	CN-MV	0.80

4.4 Conclusions

Reduction potentials for a range of stable organic radicals have been calculated. They lie over a wide window from +2.3 V to -2.4 V. The highest reduction potential of diphosphine (+2.3 V) is due to its dicationic charge and weak π-bond, which provide an electropositive and delocalisable space for the additional electron to occupy. The lowest reduction potential of t-butyl nitroxide (-2.4 V) is due to the strong oxoammonium π-bond which forms and the reasonably strong inductive electron donation through the two adjacent N-C σ-bonds. Such molecules are promising for designing high-voltage organic batteries. Of the 666 cells studied, 249 store energy within the optimal Shockley-Quiesser range of 0.8–2.0 eV and make for good candidates for photorechargeable organic batteries.

Chapter 5

Conclusions and future work

Chemical substitution can be effectively used to tune redox potentials of novel redox-active organic molecules for use in high-voltage RFBs. In particular, attaching electron-donating substitutents to catholytes (electron-accepting molecules) and electron-withdrawing groups to anolytes (electron-donating molecules) is a useful strategy for maximising the redox potential difference between them. In the context of quinone-based batteries, optimal energy storage is achieved using 1,3,5,7-NH_2AQ and 2,5-NO_2BH_2Q. In the context of radical organic battery components, pairs of methyl viologens with extremely electron-donating and electron-withdrawing substitutents are a promising practical proposition.

To achieve a photorechargeable RFB, the energy required for the endothermic steps of recharging must be provided by solar radiation. Factoring in photorecharging efficiency and the total energy stored, more mild electrolytes are favoured. Pairs of quinones and hydroquinones that are singly-substituted with electron-withdrawing groups, such as 2-CNAQ and 2-$CNNH_2Q$, are promising for photorechargeable RFB design. A large number of pairs of organic radical species have cell potentials in the optimal photorecharging range of 0.8–2.0 V.

Overall, promising lead compounds for the ongoing and future development of organic battery components have been identified. Future experimental work could focus on synthesising novel compounds with advantageous redox properties, characterising their electrochemical performance and optimising their electrochemical, physicochemical and kinetic performance by tuning the experimental conditions, such as investigating different solvents, electrolytes, pH levels and proton sources.

Chapter 6

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Appendix A

Supplementary information

Table A.1: Unsubstituted charging reaction calculated using different methods at 6-311+G(2d,p)

Reaction coordinate	B3LYP	MP2	ROMP2
A + BH_2	0	0	0
$A^{\bullet -}$ + $BH_2^{\bullet +}$	591.8331	667.4868	625.3746
$AH^{\bullet}$ + $BH^{\bullet}$	188.7643	581.4960	280.8449
AH^{-} + BH^{+}	787.7517	813.0664	—
AH_2 + B	141.2452	143.6445	—

Table A.2: Values of $< S^2 >$ for unrestricted MP2/6-311+G(2d,p) calculations on unsubstituted doublet species shows significant spin contamination in the UHF wavefunctions. The expected value for a doublet species is 0.75.

Species	UMP2	UB3LYP
$A^{\bullet -}$	0.8472	0.7583
$AH^{\bullet}$	2.0719	0.7751
$BH_2^{\bullet +}$	0.8015	0.7570
$BH^{\bullet}$	1.3412	0.7763

Unrestricted methods, such as B3LYP, are less susceptible to spin contamination for radical species.[38] This results in the energies of doublet species calculated by UMP2 and B3LYP being significantly different. B3LYP results align well with the high-quality (RO)MP2 calculations for all species.

Appendix B

Thermodynamic parameters of coupled quinones

This chapter contains tables of calculated thermodynamic parameters (ΔE_1, ΔE_2, ΔE_{stored} and P) for pairs of hydroquinones (columns) and quinones (rows). For each substitution pattern, different quinones are listed in order of increasing electron-withdrawal due to substitution.

B.1 Energy stored

Table B.1: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of benzohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised BH_2Q	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	2,5-NH_2	2,5-OH	2,5-CH_3	2,5-CN	2,5-NO_2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.2437	1.2248	1.2275	1.2325	1.248	1.2524	1.195	1.2142	1.2273	1.2543	1.2625
Benzoquinones												
H	-1.2437	0	-0.5122	-0.4395	-0.3028	0.1175	0.2384	-1.3228	-0.8011	-0.4454	0.289	0.5118
2-NH_2	-1.2248	0.5122	0	0.0728	0.2094	0.6297	0.7506	-0.8106	-0.2889	0.0669	0.8013	1.024
2-OH	-1.2275	0.4395	-0.0728	0	0.1367	0.5569	0.6779	-0.8833	-0.3616	-0.0059	0.7285	0.9512
2-CH_3	-1.2325	0.3028	-0.2094	-0.1367	0	0.4203	0.5412	-1.02	-0.4983	-0.1425	0.5918	0.8146
2-CN	-1.248	-0.1175	-0.6297	-0.5569	-0.4203	0	0.1209	-1.4403	-0.9186	-0.5628	0.1716	0.3943
2-NO_2	-1.2524	-0.2384	-0.7506	-0.6779	-0.5412	-0.1209	0	-1.5612	-1.0395	-0.6837	0.0506	0.2734
2,5-NH_2	-1.195	1.3228	0.8106	0.8833	1.02	1.4403	1.5612	0	0.5217	0.8775	1.6118	1.8346
2,5-OH	-1.2142	0.8011	0.2889	0.3616	0.4983	0.9186	1.0395	-0.5217	0	0.3557	1.0901	1.3128
2,5-CH_3	-1.2273	0.4454	-0.0669	0.0059	0.1425	0.5628	0.6837	-0.8775	-0.3557	0	0.7344	0.9571
2,5-CN	-1.2543	-0.289	-0.8013	-0.7285	-0.5918	-0.1716	-0.0506	-1.6118	-1.0901	-0.7344	0	0.2227
2,5-NO_2	-1.2625	-0.5118	-1.024	-0.9512	-0.8146	-0.3943	-0.2734	-1.8346	-1.3128	-0.9571	-0.2227	0
Naphthoquinones												
H	-1.2256	0.4904	-0.0219	0.0509	0.1876	0.6078	0.7288	-0.8324	-0.3107	0.045	0.7794	1.0021
2-NH_2	-1.1993	1.2076	0.6954	0.7682	0.9048	1.3251	1.446	-0.1152	0.4065	0.7623	1.4967	1.7194
2-OH	-1.2067	1.0053	0.493	0.5658	0.7025	1.1227	1.2437	-0.3175	0.2042	0.5599	1.2943	1.517
2-CH_3	-1.2105	0.9013	0.3891	0.4619	0.5985	1.0188	1.1397	-0.4215	0.1002	0.456	1.1904	1.4131
2-CN	-1.2476	-0.1063	-0.6186	-0.5458	-0.4092	0.0111	0.132	-1.4292	-0.9074	-0.5517	0.1827	0.4054
2-NO_2	-1.2295	0.3861	-0.1262	-0.0534	0.0833	0.5036	0.6245	-0.9367	-0.415	-0.0593	0.6751	0.8978
5-NH_2	-1.2082	0.9658	0.4536	0.5264	0.663	1.0833	1.2042	-0.357	0.1648	0.5205	1.2549	1.4776
5-OH	-1.2121	0.8583	0.3461	0.4188	0.5555	0.9758	1.0967	-0.4645	0.0572	0.4129	1.1473	1.37
5-CH_3	-1.2123	0.8523	0.34	0.4128	0.5495	0.9698	1.0907	-0.4705	0.0512	0.4069	1.1413	1.364
5-CN	-1.2191	0.668	0.1557	0.2285	0.3652	0.7855	0.9064	-0.6548	-0.1331	0.2226	0.957	1.1797
5-NO_2	-1.2238	0.539	0.0267	0.0995	0.2362	0.6565	0.7774	-0.7838	-0.2621	0.0936	0.828	1.0507
6-NH_2	-1.2103	0.9073	0.395	0.4678	0.6045	1.0248	1.1457	-0.4155	0.1062	0.4619	1.1963	1.419
6-OH	-1.2134	0.8225	0.3102	0.383	0.5197	0.9399	1.0609	-0.5003	0.0214	0.3771	1.1115	1.3342
6-CH_3	-1.2138	0.8133	0.3011	0.3738	0.5105	0.9308	1.0517	-0.5095	0.0122	0.3679	1.1023	1.3251
6-CN	-1.2215	0.603	0.0908	0.1635	0.3002	0.7205	0.8414	-0.7198	-0.1981	0.1576	0.892	1.1147
6-NO_2	-1.2244	0.5235	0.0113	0.0841	0.2207	0.641	0.7619	-0.7993	-0.2776	0.0782	0.8126	1.0353
2,5,7-NH_2	-1.191	1.4329	0.9207	0.9935	1.1301	1.5504	1.6713	0.1101	0.6319	0.9876	1.722	1.9447
2,5,7-OH	-1.2115	0.8746	0.3624	0.4352	0.5718	0.9921	1.113	-0.4482	0.0736	0.4293	1.1637	1.3864
2,5,7-CH_3	-1.2159	0.7557	0.2435	0.3162	0.4529	0.8732	0.9941	-0.5671	-0.0454	0.3104	1.0447	1.2675
2,5,7-CN	-1.2423	0.0375	-0.4748	-0.402	-0.2653	0.155	0.2759	-1.2853	-0.7636	-0.4079	0.3265	0.5492
2,5,7-NO_2	-1.2425	0.0325	-0.4798	-0.407	-0.2703	0.1499	0.2708	-1.2903	-0.7686	-0.4129	0.3215	0.5442
2,5,8-NH_2	-1.1832	1.6464	1.1341	1.2069	1.3436	1.7638	1.8848	0.3236	0.8453	1.201	1.9354	2.1581
2,5,8-OH	-1.207	0.9976	0.4854	0.5581	0.6948	1.1151	1.236	-0.3252	0.1965	0.5523	1.2866	1.5094
2,5,8-CH_3	-1.2133	0.8247	0.3125	0.3852	0.5219	0.9422	1.0631	-0.4981	0.0236	0.3793	1.1137	1.3365
2,5,8-CN	-1.2397	0.1076	-0.4046	-0.3319	-0.1952	0.2251	0.346	-1.2152	-0.6935	-0.3378	0.3966	0.6194
2,5,8-NO_2	-1.2523	-0.2351	-0.7473	-0.6745	-0.5379	-0.1176	0.0033	-1.5579	-1.0361	-0.6804	0.054	0.2767
2,6,8-NH_2	-1.1796	1.7417	1.2295	1.3023	1.4389	1.8592	1.9801	0.4189	0.9406	1.2964	2.0308	2.2535
2,6,8-OH	-1.206	1.0257	0.5135	0.5862	0.7229	1.1432	1.2641	-0.2971	0.2246	0.5804	1.3147	1.5375
2,6,8-CH_3	-1.2152	0.7748	0.2626	0.3354	0.472	0.8923	1.0132	-0.548	-0.0262	0.3295	1.0639	1.2866
2,6,8-CN	-1.242	0.0463	-0.4659	-0.3931	-0.2565	0.1638	0.2847	-1.2765	-0.7547	-0.399	0.3354	0.5581
2,6,8-NO_2	-1.2551	-0.3108	-0.823	-0.7503	-0.6136	-0.1933	-0.0724	-1.6336	-1.1119	-0.7562	-0.0218	0.201
Anthraquinones												
H	-1.1973	1.2604	0.7482	0.821	0.9576	1.3779	1.4988	-0.0624	0.4593	0.8151	1.5495	1.7722
1-NH_2	-1.1756	1.853	1.3408	1.4135	1.5502	1.9705	2.0914	0.5302	1.0519	1.4076	2.142	2.3648
1-OH	-1.1796	1.7436	1.2314	1.3042	1.4408	1.8611	1.982	0.4208	0.9425	1.2983	2.0327	2.2554
1-CH_3	-1.2184	0.6866	0.1744	0.2472	0.3838	0.8041	0.925	-0.6362	-0.1144	0.2413	0.9757	1.1984
1-CN	-1.1908	1.4371	0.9249	0.9977	1.1343	1.5546	1.6755	0.1143	0.6361	0.9918	1.7262	1.9489
1-NO_2	-1.1927	1.3867	0.8744	0.9472	1.0839	1.5042	1.6251	0.0639	0.5856	0.9413	1.6757	1.8984
2-NH_2	-1.1794	1.748	1.2358	1.3086	1.4452	1.8655	1.9864	0.4252	0.9469	1.3027	2.0371	2.2598
2-OH	-1.1824	1.6676	1.1554	1.2281	1.3648	1.7851	1.906	0.3448	0.8665	1.2223	1.9566	2.1794
2-CH_3	-1.1827	1.6596	1.1474	1.2202	1.3568	1.7771	1.898	0.3368	0.8585	1.2143	1.9487	2.1714
2-CN	-1.1915	1.4197	0.9074	0.9802	1.1169	1.5371	1.6581	0.0969	0.6186	0.9743	1.7087	1.9314
2-NO_2	-1.1939	1.3528	0.8405	0.9133	1.05	1.4702	1.5912	0.03	0.5517	0.9074	1.6418	1.8645
1,3,5,7-NH_2	-1.1639	2.1702	1.6579	1.7307	1.8674	2.2876	2.4085	0.8474	1.3691	1.7248	2.4592	2.6819
1,3,5,7-OH	-1.1862	1.5647	1.0525	1.1252	1.2619	1.6822	1.8031	0.2419	0.7636	1.1194	1.8537	2.0765
1,3,5,7-CH_3	-1.1871	1.5395	1.0273	1.1	1.2367	1.657	1.7779	0.2167	0.7384	1.0941	1.8285	2.0512
1,3,5,7-CN	-1.2129	0.8359	0.3237	0.3964	0.5331	0.9534	1.0743	-0.4869	0.0348	0.3905	1.1249	1.3476
1,3,5,7-NO_2	-1.2216	0.6008	0.0886	0.1613	0.298	0.7183	0.8392	-0.722	-0.2003	0.1555	0.8898	1.1126

Table B.2: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	H	2-NH2	2-OH	2-CH3	2-CN	2-NO2	5-NH2	5-OH	5-CH3	5-CN	5-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.2256	1.1993	1.2067	1.2105	1.2476	1.2295	1.2082	1.2121	1.2123	1.2191	1.2238
Benzoquinones												
H	-1.2437	-0.4904	-1.2076	-1.0053	-0.9013	0.1063	-0.3861	-0.9658	-0.8583	-0.8523	-0.668	-0.539
2-NH2	-1.2248	0.0219	-0.6954	-0.493	-0.3891	0.6186	0.1262	-0.4536	-0.3461	-0.34	-0.1557	-0.0267
2-OH	-1.2275	-0.0509	-0.7682	-0.5658	-0.4619	0.5458	0.0534	-0.5264	-0.4188	-0.4128	-0.2285	-0.0995
2-CH3	-1.2325	-0.1876	-0.9048	-0.7025	-0.5985	0.4092	-0.0833	-0.663	-0.5555	-0.5495	-0.3652	-0.2362
2-CN	-1.248	-0.6078	-1.3251	-1.1227	-1.0188	-0.0111	-0.5036	-1.0833	-0.9758	-0.9698	-0.7855	-0.6565
2-NO2	-1.2524	-0.7288	-1.446	-1.2437	-1.1397	-0.132	-0.6245	-1.2042	-1.0967	-1.0907	-0.9064	-0.7774
2,5-NH2	-1.195	0.8324	0.1152	0.3175	0.4215	1.4292	0.9367	0.357	0.4645	0.4705	0.6548	0.7838
2,5-OH	-1.2142	0.3107	-0.4065	-0.2042	-0.1002	0.9074	0.415	-0.1648	-0.0572	-0.0512	0.1331	0.2621
2,5-CH3	-1.2273	-0.045	-0.7623	-0.5599	-0.456	0.5517	0.0593	-0.5205	-0.4129	-0.4069	-0.2226	-0.0936
2,5-CN	-1.2543	-0.7794	-1.4967	-1.2943	-1.1904	-0.1827	-0.6751	-1.2549	-1.1473	-1.1413	-0.957	-0.828
2,5-NO2	-1.2625	-1.0021	-1.7194	-1.517	-1.4131	-0.4054	-0.8978	-1.4776	-1.37	-1.364	-1.1797	-1.0507
Naphthoquinones												
H	-1.2256	0	-0.7173	-0.5149	-0.411	0.5967	0.1043	-0.4755	-0.3679	-0.3619	-0.1776	-0.0486
2-NH2	-1.1993	0.7173	0	0.2024	0.3063	1.314	0.8215	0.2418	0.3493	0.3553	0.5396	0.6687
2-OH	-1.2067	0.5149	-0.2024	0	0.1039	1.1116	0.6192	0.0394	0.147	0.153	0.3373	0.4663
2-CH3	-1.2105	0.411	-0.3063	-0.1039	0	1.0077	0.5152	-0.0645	0.043	0.049	0.2333	0.3624
2-CN	-1.2476	-0.5967	-1.314	-1.1116	-1.0077	0	-0.4924	-1.0722	-0.9646	-0.9586	-0.7743	-0.6453
2-NO2	-1.2295	-0.1043	-0.8215	-0.6192	-0.5152	0.4924	0	-0.5798	-0.4722	-0.4662	-0.2819	-0.1529
5-NH2	-1.2082	0.4755	-0.2418	-0.0394	0.0645	1.0722	0.5798	0	0.1076	0.1136	0.2979	0.4269
5-OH	-1.2121	0.3679	-0.3493	-0.147	-0.043	0.9646	0.4722	-0.1076	0	0.006	0.1903	0.3193
5-CH3	-1.2123	0.3619	-0.3553	-0.153	-0.049	0.9586	0.4662	-0.1136	-0.006	0	0.1843	0.3133
5-CN	-1.2191	0.1776	-0.5396	-0.3373	-0.2333	0.7743	0.2819	-0.2979	-0.1903	-0.1843	0	0.129
5-NO2	-1.2238	0.0486	-0.6687	-0.4663	-0.3624	0.6453	0.1529	-0.4269	-0.3193	-0.3133	-0.129	0
6-NH2	-1.2103	0.4169	-0.3004	-0.098	0.0059	1.0136	0.5212	-0.0586	0.049	0.055	0.2393	0.3683
6-OH	-1.2134	0.3321	-0.3852	-0.1828	-0.0789	0.9288	0.4364	-0.1434	-0.0358	-0.0298	0.1545	0.2835
6-CH3	-1.2138	0.3229	-0.3943	-0.192	-0.088	0.9196	0.4272	-0.1525	-0.045	-0.039	0.1453	0.2743
6-CN	-1.2215	0.1126	-0.6046	-0.4023	-0.2983	0.7093	0.2169	-0.3629	-0.2553	-0.2493	-0.065	0.064
6-NO2	-1.2244	0.0331	-0.6841	-0.4817	-0.3778	0.6299	0.1374	-0.4423	-0.3348	-0.3288	-0.1445	-0.0155
2,5,7-NH2	-1.191	0.9426	0.2253	0.4277	0.5316	1.5393	1.0469	0.4671	0.5747	0.5807	0.765	0.894
2,5,7-OH	-1.2115	0.3843	-0.333	-0.1306	-0.0267	0.981	0.4886	-0.0912	0.0164	0.0224	0.2067	0.3357
2,5,7-CH3	-1.2159	0.2653	-0.4519	-0.2496	-0.1456	0.8621	0.3696	-0.2101	-0.1026	-0.0966	0.0877	0.2167
2,5,7-CN	-1.2423	-0.4529	-1.1701	-0.9678	-0.8638	0.1438	-0.3486	-0.9284	-0.8208	-0.8148	-0.6305	-0.5015
2,5,7-NO2	-1.2425	-0.4579	-1.1752	-0.9728	-0.8689	0.1388	-0.3536	-0.9334	-0.8258	-0.8198	-0.6355	-0.5065
2,5,8-NH2	-1.1832	1.156	0.4387	0.6411	0.745	1.7527	1.2603	0.6805	0.7881	0.7941	0.9784	1.1074
2,5,8-OH	-1.207	0.5072	-0.21	-0.0077	0.0963	1.104	0.6115	0.0318	0.1393	0.1453	0.3296	0.4586
2,5,8-CH3	-1.2133	0.3343	-0.3829	-0.1806	-0.0766	0.931	0.4386	-0.1412	-0.0336	-0.0276	0.1567	0.2857
2,5,8-CN	-1.2397	-0.3828	-1.1	-0.8977	-0.7937	0.2139	-0.2785	-0.8582	-0.7507	-0.7447	-0.5604	-0.4314
2,5,8-NO2	-1.2523	-0.7254	-1.4427	-1.2403	-1.1364	-0.1287	-0.6211	-1.2009	-1.0933	-1.0873	-0.903	-0.774
2,6,8-NH2	-1.1796	1.2514	0.5341	0.7365	0.8404	1.8481	1.3556	0.7759	0.8834	0.8894	1.0737	1.2028
2,6,8-OH	-1.206	0.5353	-0.1819	0.0204	0.1244	1.1321	0.6396	0.0599	0.1674	0.1734	0.3577	0.4867
2,6,8-CH3	-1.2152	0.2845	-0.4328	-0.2304	-0.1265	0.8812	0.3888	-0.191	-0.0834	-0.0774	0.1069	0.2359
2,6,8-CN	-1.242	-0.444	-1.1613	-0.9589	-0.855	0.1527	-0.3397	-0.9195	-0.8119	-0.8059	-0.6216	-0.4926
2,6,8-NO2	-1.2551	-0.8012	-1.5184	-1.3161	-1.2121	-0.2045	-0.6969	-1.2767	-1.1691	-1.1631	-0.9788	-0.8498
Anthraquinones												
H	-1.1973	0.77	0.0528	0.2552	0.3591	1.3668	0.8743	0.2946	0.4021	0.4081	0.5924	0.7214
1-NH2	-1.1756	1.3626	0.6454	0.8477	0.9517	1.9593	1.4669	0.8871	0.9947	1.0007	1.185	1.314
1-OH	-1.1796	1.2533	0.536	0.7384	0.8423	1.85	1.3575	0.7778	0.8853	0.8913	1.0756	1.2046
1-CH3	-1.2184	0.1963	-0.521	-0.3186	-0.2147	0.793	0.3006	-0.2792	-0.1716	-0.1656	0.0187	0.1477
1-CN	-1.1908	0.9468	0.2295	0.4319	0.5358	1.5435	1.0511	0.4713	0.5789	0.5849	0.7692	0.8982
1-NO2	-1.1927	0.8963	0.1791	0.3814	0.4854	1.493	1.0006	0.4208	0.5284	0.5344	0.7187	0.8477
2-NH2	-1.1794	1.2577	0.5404	0.7428	0.8467	1.8544	1.3619	0.7822	0.8897	0.8958	1.0801	1.2091
2-OH	-1.1824	1.1772	0.46	0.6623	0.7663	1.774	1.2815	0.7018	0.8093	0.8153	0.9996	1.1286
2-CH3	-1.1827	1.1693	0.452	0.6544	0.7583	1.766	1.2735	0.6938	0.8013	0.8073	0.9916	1.1207
2-CN	-1.1915	0.9293	0.212	0.4144	0.5183	1.526	1.0336	0.4538	0.5614	0.5674	0.7517	0.8807
2-NO2	-1.1939	0.8624	0.1451	0.3475	0.4514	1.4591	0.9667	0.3869	0.4945	0.5005	0.6848	0.8138
1,3,5,7-NH2	-1.1639	1.6798	0.9625	1.1649	1.2688	2.2765	1.7841	1.2043	1.3119	1.3179	1.5022	1.6312
1,3,5,7-OH	-1.1862	1.0743	0.3571	0.5594	0.6634	1.6711	1.1786	0.5989	0.7064	0.7124	0.8967	1.0257
1,3,5,7-CH3	-1.1871	1.0491	0.3319	0.5342	0.6382	1.6458	1.1534	0.5736	0.6812	0.6872	0.8715	1.0005
1,3,5,7-CN	-1.2129	0.3455	-0.3717	-0.1694	-0.0654	0.9422	0.4498	-0.13	-0.0224	-0.0164	0.1679	0.2969
1,3,5,7-NO2	-1.2216	0.1104	-0.6068	-0.4045	-0.3005	0.7072	0.2147	-0.365	-0.2575	-0.2515	-0.0672	0.0618

Table B.3: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of napthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	6-NH2	6-OH	6-CH3	6-CN	6-NO2	2,5,7-NH2	2,5,7-OH	2,5,7-CH3	2,5,7-CN	2,5,7-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.2103	1.2134	1.2138	1.2215	1.2244	1.191	1.2115	1.2159	1.2423	1.2425
Benzoquinones											
H	-1.2437	-0.9073	-0.8225	-0.8133	-0.603	-0.5235	-1.4329	-0.8746	-0.7557	-0.0375	-0.0325
2-NH2	-1.2248	-0.395	-0.3102	-0.3011	-0.0908	-0.0113	-0.9207	-0.3624	-0.2435	0.4748	0.4798
2-OH	-1.2275	-0.4678	-0.383	-0.3738	-0.1635	-0.0841	-0.9935	-0.4352	-0.3162	0.402	0.407
2-CH3	-1.2325	-0.6045	-0.5197	-0.5105	-0.3002	-0.2207	-1.1301	-0.5718	-0.4529	0.2653	0.2703
2-CN	-1.248	-1.0248	-0.9399	-0.9308	-0.7205	-0.641	-1.5504	-0.9921	-0.8732	-0.155	-0.1499
2-NO2	-1.2524	-1.1457	-1.0609	-1.0517	-0.8414	-0.7619	-1.6713	-1.113	-0.9941	-0.2759	-0.2708
2,5-NH2	-1.195	0.4155	0.5003	0.5095	0.7198	0.7993	-0.1101	0.4482	0.5671	1.2853	1.2903
2,5-OH	-1.2142	-0.1062	-0.0214	-0.0122	0.1981	0.2776	-0.6319	-0.0736	0.0454	0.7636	0.7686
2,5-CH3	-1.2273	-0.4619	-0.3771	-0.3679	-0.1576	-0.0782	-0.9876	-0.4293	-0.3104	0.4079	0.4129
2,5-CN	-1.2543	-1.1963	-1.1115	-1.1023	-0.892	-0.8126	-1.722	-1.1637	-1.0447	-0.3265	-0.3215
2,5-NO2	-1.2625	-1.419	-1.3342	-1.3251	-1.1147	-1.0353	-1.9447	-1.3864	-1.2675	-0.5492	-0.5442
Naphthoquinones											
H	-1.2256	-0.4169	-0.3321	-0.3229	-0.1126	-0.0331	-0.9426	-0.3843	-0.2653	0.4529	0.4579
2-NH2	-1.1993	0.3004	0.3852	0.3943	0.6046	0.6841	-0.2253	0.333	0.4519	1.1701	1.1752
2-OH	-1.2067	0.098	0.1828	0.192	0.4023	0.4817	-0.4277	0.1306	0.2496	0.9678	0.9728
2-CH3	-1.2105	-0.0059	0.0789	0.088	0.2983	0.3778	-0.5316	0.0267	0.1456	0.8638	0.8689
2-CN	-1.2476	-1.0136	-0.9288	-0.9196	-0.7093	-0.6299	-1.5393	-0.981	-0.8621	-0.1438	-0.1388
2-NO2	-1.2295	-0.5212	-0.4364	-0.4272	-0.2169	-0.1374	-1.0469	-0.4886	-0.3696	0.3486	0.3536
5-NH2	-1.2082	0.0586	0.1434	0.1525	0.3629	0.4423	-0.4671	0.0912	0.2101	0.9284	0.9334
5-OH	-1.2121	-0.049	0.0358	0.045	0.2553	0.3348	-0.5747	-0.0164	0.1026	0.8208	0.8258
5-CH3	-1.2123	-0.055	0.0298	0.039	0.2493	0.3288	-0.5807	-0.0224	0.0966	0.8148	0.8198
5-CN	-1.2191	-0.2393	-0.1545	-0.1453	0.065	0.1445	-0.765	-0.2067	-0.0877	0.6305	0.6355
5-NO2	-1.2238	-0.3683	-0.2835	-0.2743	-0.064	0.0155	-0.894	-0.3357	-0.2167	0.5015	0.5065
6-NH2	-1.2103	0	0.0848	0.094	0.3043	0.3838	-0.5257	0.0326	0.1516	0.8698	0.8748
6-OH	-1.2134	-0.0848	0	0.0092	0.2195	0.2989	-0.6105	-0.0522	0.0668	0.785	0.79
6-CH3	-1.2138	-0.094	-0.0092	0	0.2103	0.2898	-0.6196	-0.0613	0.0576	0.7758	0.7808
6-CN	-1.2215	-0.3043	-0.2195	-0.2103	0	0.0795	-0.83	-0.2717	-0.1527	0.5655	0.5705
6-NO2	-1.2244	-0.3838	-0.2989	-0.2898	-0.0795	0	-0.9094	-0.3511	-0.2322	0.486	0.4911
2,5,7-NH2	-1.191	0.5257	0.6105	0.6196	0.83	0.9094	0	0.5583	0.6772	1.3955	1.4005
2,5,7-OH	-1.2115	-0.0326	0.0522	0.0613	0.2717	0.3511	-0.5583	0	0.1189	0.8372	0.8422
2,5,7-CH3	-1.2159	-0.1516	-0.0668	-0.0576	0.1527	0.2322	-0.6772	-0.1189	0	0.7182	0.7232
2,5,7-CN	-1.2423	-0.8698	-0.785	-0.7758	-0.5655	-0.486	-1.3955	-0.8372	-0.7182	0	0.005
2,5,7-NO2	-1.2425	-0.8748	-0.79	-0.7808	-0.5705	-0.4911	-1.4005	-0.8422	-0.7232	-0.005	0
2,5,8-NH2	-1.1832	0.7391	0.8239	0.8331	1.0434	1.1228	0.2134	0.7717	0.8907	1.6089	1.6139
2,5,8-OH	-1.207	0.0903	0.1751	0.1843	0.3946	0.4741	-0.4353	0.123	0.2419	0.9601	0.9652
2,5,8-CH3	-1.2133	-0.0826	0.0022	0.0114	0.2217	0.3012	-0.6083	-0.05	0.069	0.7872	0.7922
2,5,8-CN	-1.2397	-0.7997	-0.7149	-0.7057	-0.4954	-0.4159	-1.3253	-0.767	-0.6481	0.0701	0.0751
2,5,8-NO2	-1.2523	-1.1423	-1.0575	-1.0484	-0.838	-0.7586	-1.668	-1.1097	-0.9908	-0.2725	-0.2675
2,6,8-NH2	-1.1796	0.8345	0.9193	0.9284	1.1387	1.2182	0.3088	0.8671	0.986	1.7042	1.7093
2,6,8-OH	-1.206	0.1184	0.2032	0.2124	0.4227	0.5022	-0.4072	0.1511	0.27	0.9882	0.9932
2,6,8-CH3	-1.2152	-0.1324	-0.0476	-0.0385	0.1719	0.2513	-0.6581	-0.0998	0.0191	0.7374	0.7424
2,6,8-CN	-1.242	-0.8609	-0.7761	-0.767	-0.5566	-0.4772	-1.3866	-0.8283	-0.7094	0.0089	0.0139
2,6,8-NO2	-1.2551	-1.2181	-1.1333	-1.1241	-0.9138	-0.8343	-1.7438	-1.1855	-1.0665	-0.3483	-0.3433
Anthraquinones											
H	-1.1973	0.3531	0.438	0.4471	0.6574	0.7369	-0.1725	0.3858	0.5047	1.2229	1.228
1-NH2	-1.1756	0.9457	1.0305	1.0397	1.25	1.3295	0.42	0.9784	1.0973	1.8155	1.8205
1-OH	-1.1796	0.8363	0.9212	0.9303	1.1406	1.2201	0.3107	0.869	0.9879	1.7061	1.7112
1-CH3	-1.2184	-0.2206	-0.1358	-0.1267	0.0837	0.1631	-0.7463	-0.188	-0.0691	0.6492	0.6542
1-CN	-1.1908	0.5299	0.6147	0.6238	0.8342	0.9136	0.0042	0.5625	0.6814	1.3997	1.4047
1-NO2	-1.1927	0.4794	0.5642	0.5734	0.7837	0.8632	-0.0463	0.512	0.631	1.3492	1.3542
2-NH2	-1.1794	0.8408	0.9256	0.9347	1.145	1.2245	0.3151	0.8734	0.9923	1.7105	1.7156
2-OH	-1.1824	0.7603	0.8451	0.8543	1.0646	1.1441	0.2347	0.793	0.9119	1.6301	1.6351
2-CH3	-1.1827	0.7524	0.8372	0.8463	1.0566	1.1361	0.2267	0.785	0.9039	1.6221	1.6272
2-CN	-1.1915	0.5124	0.5972	0.6064	0.8167	0.8961	-0.0133	0.545	0.664	1.3822	1.3872
2-NO2	-1.1939	0.4455	0.5303	0.5395	0.7498	0.8292	-0.0802	0.4781	0.5971	1.3153	1.3203
1,3,5,7-NH2	-1.1639	1.2629	1.3477	1.3569	1.5672	1.6466	0.7372	1.2955	1.4144	2.1327	2.1377
1,3,5,7-OH	-1.1862	0.6574	0.7422	0.7514	0.9617	1.0412	0.1318	0.6901	0.809	1.5272	1.5323
1,3,5,7-CH3	-1.1871	0.6322	0.717	0.7262	0.9365	1.016	0.1065	0.6648	0.7838	1.502	1.507
1,3,5,7-CN	-1.2129	-0.0714	0.0134	0.0226	0.2329	0.3124	-0.5971	-0.0388	0.0802	0.7984	0.8034
1,3,5,7-NO2	-1.2216	-0.3065	-0.2217	-0.2125	-0.0022	0.0773	-0.8321	-0.2738	-0.1549	0.5633	0.5683

Table B.4: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of napthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	2,5,8-NH2	2,5,8-OH	2,5,8-CH3	2,5,8-CN	2,5,8-NO2	2,6,8-NH2	2,6,8-OH	2,6,8-CH3	2,6,8-CN	2,6,8-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.1832	1.207	1.2133	1.2397	1.2523	1.1796	1.206	1.2152	1.242	1.2551
Benzoquinones											
H	-1.2437	-1.6464	-0.9976	-0.8247	-0.1076	0.2351	-1.7417	-1.0257	-0.7748	-0.0463	0.3108
2-NH2	-1.2248	-1.1341	-0.4854	-0.3125	0.4046	0.7473	-1.2295	-0.5135	-0.2626	0.4659	0.823
2-OH	-1.2275	-1.2069	-0.5581	-0.3852	0.3319	0.6745	-1.3023	-0.5862	-0.3354	0.3931	0.7503
2-CH3	-1.2325	-1.3436	-0.6948	-0.5219	0.1952	0.5379	-1.4389	-0.7229	-0.472	0.2565	0.6136
2-CN	-1.248	-1.7638	-1.1151	-0.9422	-0.2251	0.1176	-1.8592	-1.1432	-0.8923	-0.1638	0.1933
2-NO2	-1.2524	-1.8848	-1.236	-1.0631	-0.346	-0.0033	-1.9801	-1.2641	-1.0132	-0.2847	0.0724
2,5-NH2	-1.195	-0.3236	0.3252	0.4981	1.2152	1.5579	-0.4189	0.2971	0.548	1.2765	1.6336
2,5-OH	-1.2142	-0.8453	-0.1965	-0.0236	0.6935	1.0361	-0.9406	-0.2246	0.0262	0.7547	1.1119
2,5-CH3	-1.2273	-1.201	-0.5523	-0.3793	0.3378	0.6804	-1.2964	-0.5804	-0.3295	0.399	0.7562
2,5-CN	-1.2543	-1.9354	-1.2866	-1.1137	-0.3966	-0.054	-2.0308	-1.3147	-1.0639	-0.3354	0.0218
2,5-NO2	-1.2625	-2.1581	-1.5094	-1.3365	-0.6194	-0.2767	-2.2535	-1.5375	-1.2866	-0.5581	-0.201
Naphthoquinones											
H	-1.2256	-1.156	-0.5072	-0.3343	0.3828	0.7254	-1.2514	-0.5353	-0.2845	0.444	0.8012
2-NH2	-1.1993	-0.4387	0.21	0.3829	1.1	1.4427	-0.5341	0.1819	0.4328	1.1613	1.5184
2-OH	-1.2067	-0.6411	0.0077	0.1806	0.8977	1.2403	-0.7365	-0.0204	0.2304	0.9589	1.3161
2-CH3	-1.2105	-0.745	-0.0963	0.0766	0.7937	1.1364	-0.8404	-0.1244	0.1265	0.855	1.2121
2-CN	-1.2476	-1.7527	-1.104	-0.931	-0.2139	0.1287	-1.8481	-1.1321	-0.8812	-0.1527	0.2045
2-NO2	-1.2295	-1.2603	-0.6115	-0.4386	0.2785	0.6211	-1.3556	-0.6396	-0.3888	0.3397	0.6969
5-NH2	-1.2082	-0.6805	-0.0318	0.1412	0.8582	1.2009	-0.7759	-0.0599	0.191	0.9195	1.2767
5-OH	-1.2121	-0.7881	-0.1393	0.0336	0.7507	1.0933	-0.8834	-0.1674	0.0834	0.8119	1.1691
5-CH3	-1.2123	-0.7941	-0.1453	0.0276	0.7447	1.0873	-0.8894	-0.1734	0.0774	0.8059	1.1631
5-CN	-1.2191	-0.9784	-0.3296	-0.1567	0.5604	0.903	-1.0737	-0.3577	-0.1069	0.6216	0.9788
5-NO2	-1.2238	-1.1074	-0.4586	-0.2857	0.4314	0.774	-1.2028	-0.4867	-0.2359	0.4926	0.8498
6-NH2	-1.2103	-0.7391	-0.0903	0.0826	0.7997	1.1423	-0.8345	-0.1184	0.1324	0.8609	1.2181
6-OH	-1.2134	-0.8239	-0.1751	-0.0022	0.7149	1.0575	-0.9193	-0.2032	0.0476	0.7761	1.1333
6-CH3	-1.2138	-0.8331	-0.1843	-0.0114	0.7057	1.0484	-0.9284	-0.2124	0.0385	0.767	1.1241
6-CN	-1.2215	-1.0434	-0.3946	-0.2217	0.4954	0.838	-1.1387	-0.4227	-0.1719	0.5566	0.9138
6-NO2	-1.2244	-1.1228	-0.4741	-0.3012	0.4159	0.7586	-1.2182	-0.5022	-0.2513	0.4772	0.8343
2,5,7-NH2	-1.191	-0.2134	0.4353	0.6083	1.3253	1.668	-0.3088	0.4072	0.6581	1.3866	1.7438
2,5,7-OH	-1.2115	-0.7717	-0.123	0.05	0.767	1.1097	-0.8671	-0.1511	0.0998	0.8283	1.1855
2,5,7-CH3	-1.2159	-0.8907	-0.2419	-0.069	0.6481	0.9908	-0.986	-0.27	-0.0191	0.7094	1.0665
2,5,7-CN	-1.2423	-1.6089	-0.9601	-0.7872	-0.0701	0.2725	-1.7042	-0.9882	-0.7374	-0.0089	0.3483
2,5,7-NO2	-1.2425	-1.6139	-0.9652	-0.7922	-0.0751	0.2675	-1.7093	-0.9932	-0.7424	-0.0139	0.3433
2,5,8-NH2	-1.1832	0	0.6488	0.8217	1.5388	1.8814	-0.0954	0.6207	0.8715	1.6	1.9572
2,5,8-OH	-1.207	-0.6488	0	0.1729	0.89	1.2327	-0.7441	-0.0281	0.2228	0.9513	1.3084
2,5,8-CH3	-1.2133	-0.8217	-0.1729	0	0.7171	1.0597	-0.917	-0.201	0.0499	0.7784	1.1355
2,5,8-CN	-1.2397	-1.5388	-0.89	-0.7171	0	0.3427	-1.6341	-0.9181	-0.6672	0.0613	0.4184
2,5,8-NO2	-1.2523	-1.8814	-1.2327	-1.0597	-0.3427	0	-1.9768	-1.2608	-1.0099	-0.2814	0.0758
2,6,8-NH2	-1.1796	0.0954	0.7441	0.917	1.6341	1.9768	0	0.716	0.9669	1.6954	2.0525
2,6,8-OH	-1.206	-0.6207	0.0281	0.201	0.9181	1.2608	-0.716	0	0.2509	0.9794	1.3365
2,6,8-CH3	-1.2152	-0.8715	-0.2228	-0.0499	0.6672	1.0099	-0.9669	-0.2509	0	0.7285	1.0856
2,6,8-CN	-1.242	-1.6	-0.9513	-0.7784	-0.0613	0.2814	-1.6954	-0.9794	-0.7285	0	0.3571
2,6,8-NO2	-1.2551	-1.9572	-1.3084	-1.1355	-0.4184	-0.0758	-2.0525	-1.3365	-1.0856	-0.3571	0
Anthraquinones											
H	-1.1973	-0.3859	0.2628	0.4357	1.1528	1.4955	-0.4813	0.2347	0.4856	1.2141	1.5712
1-NH2	-1.1756	0.2066	0.8554	1.0283	1.7454	2.0881	0.1113	0.8273	1.0782	1.8067	2.1638
1-OH	-1.1796	0.0973	0.746	0.9189	1.636	1.9787	0.0019	0.7179	0.9688	1.6973	2.0544
1-CH3	-1.2184	-0.9597	-0.311	-0.1381	0.579	0.9217	-1.0551	-0.3391	-0.0882	0.6403	0.9974
1-CN	-1.1908	-0.2092	0.4395	0.6124	1.3295	1.6722	-0.3046	0.4114	0.6623	1.3908	1.7479
1-NO2	-1.1927	-0.2597	0.3891	0.562	1.2791	1.6217	-0.3551	0.361	0.6118	1.3403	1.6975
2-NH2	-1.1794	0.1017	0.7504	0.9233	1.6404	1.9831	0.0063	0.7223	0.9732	1.7017	2.0588
2-OH	-1.1824	0.0212	0.67	0.8429	1.56	1.9027	-0.0741	0.6419	0.8928	1.6213	1.9784
2-CH3	-1.1827	0.0133	0.662	0.8349	1.552	1.8947	-0.0821	0.6339	0.8848	1.6133	1.9704
2-CN	-1.1915	-0.2267	0.4221	0.595	1.3121	1.6547	-0.3221	0.394	0.6448	1.3733	1.7305
2-NO2	-1.1939	-0.2936	0.3552	0.5281	1.2452	1.5878	-0.389	0.3271	0.5779	1.3064	1.6636
1,3,5,7-NH2	-1.1639	0.5238	1.1725	1.3455	2.0626	2.4052	0.4284	1.1445	1.3953	2.1238	2.481
1,3,5,7-OH	-1.1862	-0.0816	0.5671	0.74	1.4571	1.7998	-0.177	0.539	0.7899	1.5184	1.8755
1,3,5,7-CH3	-1.1871	-0.1069	0.5419	0.7148	1.4319	1.7745	-0.2022	0.5138	0.7646	1.4931	1.8503
1,3,5,7-CN	-1.2129	-0.8105	-0.1617	0.0112	0.7283	1.0709	-0.9058	-0.1898	0.061	0.7895	1.1467
1,3,5,7-NO2	-1.2216	-1.0456	-0.3968	-0.2239	0.4932	0.8359	-1.1409	-0.4249	-0.174	0.5545	0.9116

Table B.5: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised AH_2Q	H	1-NH2	1-OH	1-CH3	1-CN	1-NO2	2-NH2	2-OH	2-CH3	2-CN	2-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.1973	1.1756	1.1796	1.2184	1.1908	1.1927	1.1794	1.1824	1.1827	1.1915	1.1939
Benzoquinones												
H	-1.2437	-1.2604	-1.853	-1.7436	-0.6866	-1.4371	-1.3867	-1.748	-1.6676	-1.6596	-1.4197	-1.3528
2-NH2	-1.2248	-0.7482	-1.3408	-1.2314	-0.1744	-0.9249	-0.8744	-1.2358	-1.1554	-1.1474	-0.9074	-0.8405
2-OH	-1.2275	-0.821	-1.4135	-1.3042	-0.2472	-0.9977	-0.9472	-1.3086	-1.2281	-1.2202	-0.9802	-0.9133
2-CH3	-1.2325	-0.9576	-1.5502	-1.4408	-0.3838	-1.1343	-1.0839	-1.4452	-1.3648	-1.3568	-1.1169	-1.05
2-CN	-1.248	-1.3779	-1.9705	-1.8611	-0.8041	-1.5546	-1.5042	-1.8655	-1.7851	-1.7771	-1.5371	-1.4702
2-NO2	-1.2524	-1.4988	-2.0914	-1.982	-0.925	-1.6755	-1.6251	-1.9864	-1.906	-1.898	-1.6581	-1.5912
2,5-NH2	-1.195	0.0624	-0.5302	-0.4208	0.6362	-0.1143	-0.0639	-0.4252	-0.3448	-0.3368	-0.0969	-0.03
2,5-OH	-1.2142	-0.4593	-1.0519	-0.9425	0.1144	-0.6361	-0.5856	-0.9469	-0.8665	-0.8585	-0.6186	-0.5517
2,5-CH3	-1.2273	-0.8151	-1.4076	-1.2983	-0.2413	-0.9918	-0.9413	-1.3027	-1.2223	-1.2143	-0.9743	-0.9074
2,5-CN	-1.2543	-1.5495	-2.142	-2.0327	-0.9757	-1.7262	-1.6757	-2.0371	-1.9566	-1.9487	-1.7087	-1.6418
2,5-NO2	-1.2625	-1.7722	-2.3648	-2.2554	-1.1984	-1.9489	-1.8984	-2.2598	-2.1794	-2.1714	-1.9314	-1.8645
Naphthoquinones												
H	-1.2256	-0.77	-1.3626	-1.2533	-0.1963	-0.9468	-0.8963	-1.2577	-1.1772	-1.1693	-0.9293	-0.8624
2-NH2	-1.1993	-0.0528	-0.6454	-0.536	0.521	-0.2295	-0.1791	-0.5404	-0.46	-0.452	-0.212	-0.1451
2-OH	-1.2067	-0.2552	-0.8477	-0.7384	0.3186	-0.4319	-0.3814	-0.7428	-0.6623	-0.6544	-0.4144	-0.3475
2-CH3	-1.2105	-0.3591	-0.9517	-0.8423	0.2147	-0.5358	-0.4854	-0.8467	-0.7663	-0.7583	-0.5183	-0.4514
2-CN	-1.2476	-1.3668	-1.9593	-1.85	-0.793	-1.5435	-1.493	-1.8544	-1.774	-1.766	-1.526	-1.4591
2-NO2	-1.2295	-0.8743	-1.4669	-1.3575	-0.3006	-1.0511	-1.0006	-1.3619	-1.2815	-1.2735	-1.0336	-0.9667
5-NH2	-1.2082	-0.2946	-0.8871	-0.7778	0.2792	-0.4713	-0.4208	-0.7822	-0.7018	-0.6938	-0.4538	-0.3869
5-OH	-1.2121	-0.4021	-0.9947	-0.8853	0.1716	-0.5789	-0.5284	-0.8897	-0.8093	-0.8013	-0.5614	-0.4945
5-CH3	-1.2123	-0.4081	-1.0007	-0.8913	0.1656	-0.5849	-0.5344	-0.8958	-0.8153	-0.8073	-0.5674	-0.5005
5-CN	-1.2191	-0.5924	-1.185	-1.0756	-0.0187	-0.7692	-0.7187	-1.0801	-0.9996	-0.9916	-0.7517	-0.6848
5-NO2	-1.2238	-0.7214	-1.314	-1.2046	-0.1477	-0.8982	-0.8477	-1.2091	-1.1286	-1.1207	-0.8807	-0.8138
6-NH2	-1.2103	-0.3531	-0.9457	-0.8363	0.2206	-0.5299	-0.4794	-0.8408	-0.7603	-0.7524	-0.5124	-0.4455
6-OH	-1.2134	-0.438	-1.0305	-0.9212	0.1358	-0.6147	-0.5642	-0.9256	-0.8451	-0.8372	-0.5972	-0.5303
6-CH3	-1.2138	-0.4471	-1.0397	-0.9303	0.1267	-0.6238	-0.5734	-0.9347	-0.8543	-0.8463	-0.6064	-0.5395
6-CN	-1.2215	-0.6574	-1.25	-1.1406	-0.0837	-0.8342	-0.7837	-1.145	-1.0646	-1.0566	-0.8167	-0.7498
6-NO2	-1.2244	-0.7369	-1.3295	-1.2201	-0.1631	-0.9136	-0.8632	-1.2245	-1.1441	-1.1361	-0.8961	-0.8292
2,5,7-NH2	-1.191	0.1725	-0.42	-0.3107	0.7463	-0.0042	0.0463	-0.3151	-0.2347	-0.2267	0.0133	0.0802
2,5,7-OH	-1.2115	-0.3858	-0.9784	-0.869	0.188	-0.5625	-0.512	-0.8734	-0.793	-0.785	-0.545	-0.4781
2,5,7-CH3	-1.2159	-0.5047	-1.0973	-0.9879	0.0691	-0.6814	-0.631	-0.9923	-0.9119	-0.9039	-0.664	-0.5971
2,5,7-CN	-1.2423	-1.2229	-1.8155	-1.7061	-0.6492	-1.3997	-1.3492	-1.7105	-1.6301	-1.6221	-1.3822	-1.3153
2,5,7-NO2	-1.2425	-1.228	-1.8205	-1.7112	-0.6542	-1.4047	-1.3542	-1.7156	-1.6351	-1.6272	-1.3872	-1.3203
2,5,8-NH2	-1.1832	0.3859	-0.2066	-0.0973	0.9597	0.2092	0.2597	-0.1017	-0.0212	-0.0133	0.2267	0.2936
2,5,8-OH	-1.207	-0.2628	-0.8554	-0.746	0.311	-0.4395	-0.3891	-0.7504	-0.67	-0.662	-0.4221	-0.3552
2,5,8-CH3	-1.2133	-0.4357	-1.0283	-0.9189	0.1381	-0.6124	-0.562	-0.9233	-0.8429	-0.8349	-0.595	-0.5281
2,5,8-CN	-1.2397	-1.1528	-1.7454	-1.636	-0.579	-1.3295	-1.2791	-1.6404	-1.56	-1.552	-1.3121	-1.2452
2,5,8-NO2	-1.2523	-1.4955	-2.0881	-1.9787	-0.9217	-1.6722	-1.6217	-1.9831	-1.9027	-1.8947	-1.6547	-1.5878
2,6,8-NH2	-1.1796	0.4813	-0.1113	-0.0019	1.0551	0.3046	0.3551	-0.0063	0.0741	0.0821	0.3221	0.389
2,6,8-OH	-1.206	-0.2347	-0.8273	-0.7179	0.3391	-0.4114	-0.361	-0.7223	-0.6419	-0.6339	-0.394	-0.3271
2,6,8-CH3	-1.2152	-0.4856	-1.0782	-0.9688	0.0882	-0.6623	-0.6118	-0.9732	-0.8928	-0.8848	-0.6448	-0.5779
2,6,8-CN	-1.242	-1.2141	-1.8067	-1.6973	-0.6403	-1.3908	-1.3403	-1.7017	-1.6213	-1.6133	-1.3733	-1.3064
2,6,8-NO2	-1.2551	-1.5712	-2.1638	-2.0544	-0.9974	-1.7479	-1.6975	-2.0588	-1.9784	-1.9704	-1.7305	-1.6636
Anthraquinones												
H	-1.1973	0	-0.5926	-0.4832	0.5738	-0.1767	-0.1263	-0.4876	-0.4072	-0.3992	-0.1592	-0.0923
1-NH2	-1.1756	0.5926	0	0.1094	1.1664	0.4159	0.4663	0.105	0.1854	0.1934	0.4333	0.5002
1-OH	-1.1796	0.4832	-0.1094	0	1.057	0.3065	0.3569	-0.0044	0.076	0.084	0.324	0.3909
1-CH3	-1.2184	-0.5738	-1.1664	-1.057	0	-0.7505	-0.7	-1.0614	-0.981	-0.973	-0.733	-0.6661
1-CN	-1.1908	0.1767	-0.4159	-0.3065	0.7505	0	0.0505	-0.3109	-0.2305	-0.2225	0.0175	0.0844
1-NO2	-1.1927	0.1263	-0.4663	-0.3569	0.7	-0.0505	0	-0.3614	-0.2809	-0.2729	-0.033	0.0339
2-NH2	-1.1794	0.4876	-0.105	0.0044	1.0614	0.3109	0.3614	0	0.0804	0.0884	0.3284	0.3953
2-OH	-1.1824	0.4072	-0.1854	-0.076	0.981	0.2305	0.2809	-0.0804	0	0.008	0.2479	0.3148
2-CH3	-1.1827	0.3992	-0.1934	-0.084	0.973	0.2225	0.2729	-0.0884	-0.008	0	0.24	0.3069
2-CN	-1.1915	0.1592	-0.4333	-0.324	0.733	-0.0175	0.033	-0.3284	-0.2479	-0.24	0	0.0669
2-NO2	-1.1939	0.0923	-0.5002	-0.3909	0.6661	-0.0844	-0.0339	-0.3953	-0.3148	-0.3069	-0.0669	0
1,3,5,7-NH2	-1.1639	0.9097	0.3172	0.4265	1.4835	0.733	0.7835	0.4221	0.5025	0.5105	0.7505	0.8174
1,3,5,7-OH	-1.1862	0.3043	-0.2883	-0.1789	0.8781	0.1276	0.178	-0.1833	-0.1029	-0.0949	0.145	0.2119
1,3,5,7-CH3	-1.1871	0.2791	-0.3135	-0.2041	0.8528	0.1023	0.1528	-0.2085	-0.1281	-0.1201	0.1198	0.1867
1,3,5,7-CN	-1.2129	-0.4245	-1.0171	-0.9077	0.1492	-0.6013	-0.5508	-0.9121	-0.8317	-0.8237	-0.5838	-0.5169
1,3,5,7-NO2	-1.2216	-0.6596	-1.2522	-1.1428	-0.0858	-0.8363	-0.7859	-1.1472	-1.0668	-1.0588	-0.8189	-0.752

Table B.6: ΔE_{stored} (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised AH_2Q	1,3,5,7-NH2	1,3,5,7-OH	1,3,5,7-CH3	1,3,5,7-CN	1,3,5,7-NO2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	1.1639	1.1862	1.1871	1.2129	1.2216
Benzoquinones						
H	-1.2437	-2.1702	-1.5647	-1.5395	-0.8359	-0.6008
2-NH2	-1.2248	-1.6579	-1.0525	-1.0273	-0.3237	-0.0886
2-OH	-1.2275	-1.7307	-1.1252	-1.1	-0.3964	-0.1613
2-CH3	-1.2325	-1.8674	-1.2619	-1.2367	-0.5331	-0.298
2-CN	-1.248	-2.2876	-1.6822	-1.657	-0.9534	-0.7183
2-NO2	-1.2524	-2.4085	-1.8031	-1.7779	-1.0743	-0.8392
2,5-NH2	-1.195	-0.8474	-0.2419	-0.2167	0.4869	0.722
2,5-OH	-1.2142	-1.3691	-0.7636	-0.7384	-0.0348	0.2003
2,5-CH3	-1.2273	-1.7248	-1.1194	-1.0941	-0.3905	-0.1555
2,5-CN	-1.2543	-2.4592	-1.8537	-1.8285	-1.1249	-0.8898
2,5-NO2	-1.2625	-2.6819	-2.0765	-2.0512	-1.3476	-1.1126
Naphthoquinones						
H	-1.2256	-1.6798	-1.0743	-1.0491	-0.3455	-0.1104
2-NH2	-1.1993	-0.9625	-0.3571	-0.3319	0.3717	0.6068
2-OH	-1.2067	-1.1649	-0.5594	-0.5342	0.1694	0.4045
2-CH3	-1.2105	-1.2688	-0.6634	-0.6382	0.0654	0.3005
2-CN	-1.2476	-2.2765	-1.6711	-1.6458	-0.9422	-0.7072
2-NO2	-1.2295	-1.7841	-1.1786	-1.1534	-0.4498	-0.2147
5-NH2	-1.2082	-1.2043	-0.5989	-0.5736	0.13	0.365
5-OH	-1.2121	-1.3119	-0.7064	-0.6812	0.0224	0.2575
5-CH3	-1.2123	-1.3179	-0.7124	-0.6872	0.0164	0.2515
5-CN	-1.2191	-1.5022	-0.8967	-0.8715	-0.1679	0.0672
5-NO2	-1.2238	-1.6312	-1.0257	-1.0005	-0.2969	-0.0618
6-NH2	-1.2103	-1.2629	-0.6574	-0.6322	0.0714	0.3065
6-OH	-1.2134	-1.3477	-0.7422	-0.717	-0.0134	0.2217
6-CH3	-1.2138	-1.3569	-0.7514	-0.7262	-0.0226	0.2125
6-CN	-1.2215	-1.5672	-0.9617	-0.9365	-0.2329	0.0022
6-NO2	-1.2244	-1.6466	-1.0412	-1.016	-0.3124	-0.0773
2,5,7-NH2	-1.191	-0.7372	-0.1318	-0.1065	0.5971	0.8321
2,5,7-OH	-1.2115	-1.2955	-0.6901	-0.6648	0.0388	0.2738
2,5,7-CH3	-1.2159	-1.4144	-0.809	-0.7838	-0.0802	0.1549
2,5,7-CN	-1.2423	-2.1327	-1.5272	-1.502	-0.7984	-0.5633
2,5,7-NO2	-1.2425	-2.1377	-1.5323	-1.507	-0.8034	-0.5683
2,5,8-NH2	-1.1832	-0.5238	0.0816	0.1069	0.8105	1.0456
2,5,8-OH	-1.207	-1.1725	-0.5671	-0.5419	0.1617	0.3968
2,5,8-CH3	-1.2133	-1.3455	-0.74	-0.7148	-0.0112	0.2239
2,5,8-CN	-1.2397	-2.0626	-1.4571	-1.4319	-0.7283	-0.4932
2,5,8-NO2	-1.2523	-2.4052	-1.7998	-1.7745	-1.0709	-0.8359
2,6,8-NH2	-1.1796	-0.4284	0.177	0.2022	0.9058	1.1409
2,6,8-OH	-1.206	-1.1445	-0.539	-0.5138	0.1898	0.4249
2,6,8-CH3	-1.2152	-1.3953	-0.7899	-0.7646	-0.061	0.174
2,6,8-CN	-1.242	-2.1238	-1.5184	-1.4931	-0.7895	-0.5545
2,6,8-NO2	-1.2551	-2.481	-1.8755	-1.8503	-1.1467	-0.9116
Anthraquinones						
H	-1.1973	-0.9097	-0.3043	-0.2791	0.4245	0.6596
1-NH2	-1.1756	-0.3172	0.2883	0.3135	1.0171	1.2522
1-OH	-1.1796	-0.4265	0.1789	0.2041	0.9077	1.1428
1-CH3	-1.2184	-1.4835	-0.8781	-0.8528	-0.1492	0.0858
1-CN	-1.1908	-0.733	-0.1276	-0.1023	0.6013	0.8363
1-NO2	-1.1927	-0.7835	-0.178	-0.1528	0.5508	0.7859
2-NH2	-1.1794	-0.4221	0.1833	0.2085	0.9121	1.1472
2-OH	-1.1824	-0.5025	0.1029	0.1281	0.8317	1.0668
2-CH3	-1.1827	-0.5105	0.0949	0.1201	0.8237	1.0588
2-CN	-1.1915	-0.7505	-0.145	-0.1198	0.5838	0.8189
2-NO2	-1.1939	-0.8174	-0.2119	-0.1867	0.5169	0.752
1,3,5,7-NH2	-1.1639	0	0.6054	0.6307	1.3343	1.5693
1,3,5,7-OH	-1.1862	-0.6054	0	0.0252	0.7288	0.9639
1,3,5,7-CH3	-1.1871	-0.6307	-0.0252	0	0.7036	0.9387
1,3,5,7-CN	-1.2129	-1.3343	-0.7288	-0.7036	0	0.2351
1,3,5,7-NO2	-1.2216	-1.5693	-0.9639	-0.9387	-0.2351	0

B.2 Energy barriers

B.2.1 First energy barrier

The following tables give the values of ΔE_1, which is the energy required to transfer an electron from a hydroquinone (XH_2Q) to a quinone (XQ) to give a hydroquinone radical cation ($XH_2Q^{\bullet +}$) and a quinone radical anion ($XQ^{\bullet -}$).

Table B.7: ΔE_1 (eV) for coupled redox reactions involving oxidation of benzohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised BH_2Q	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	2,5-NH_2	2,5-OH	2,5-CH_3	2,5-CN	2,5-NO_2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	0.2095	0.1855	0.1999	0.2019	0.2216	0.2267	0.1606	0.1892	0.1975	0.2366	0.2433
Benzoquinones												
H	-0.1464	1.7175	1.0663	1.4566	1.5103	2.0481	2.1857	0.3863	1.1650	1.3903	2.4563	2.6385
2-NH_2	-0.1330	2.0799	1.4287	1.8190	1.8727	2.4105	2.5481	0.7487	1.5274	1.7527	2.8187	3.0009
2-OH	-0.1391	1.9150	1.2638	1.6541	1.7078	2.2456	2.3832	0.5838	1.3625	1.5878	2.6538	2.8360
2-CH_3	-0.1379	1.9472	1.2960	1.6863	1.7400	2.2778	2.4154	0.6160	1.3946	1.6199	2.6860	2.8682
2-CN	-0.1667	1.1631	0.5119	0.9021	0.9559	1.4937	1.6313	-0.1681	0.6105	0.8358	1.9019	2.0841
2-NO_2	-0.1665	1.1693	0.5181	0.9083	0.9620	1.4998	1.6375	-0.1619	0.6167	0.8420	1.9080	2.0902
2,5-NH_2	-0.1339	2.0558	1.4046	1.7948	1.8485	2.3864	2.5240	0.7246	1.5032	1.7285	2.7946	2.9767
2,5-OH	-0.1350	2.0256	1.3745	1.7647	1.8184	2.3562	2.4938	0.6945	1.4731	1.6984	2.7644	2.9466
2,5-CH_3	-0.1347	2.0344	1.3832	1.7734	1.8271	2.3650	2.5026	0.7032	1.4818	1.7071	2.7732	2.9553
2,5-CN	-0.1729	0.9955	0.3443	0.7345	0.7883	1.3261	1.4637	-0.3357	0.4429	0.6682	1.7343	1.9164
2,5-NO_2	-0.1826	0.7315	0.0803	0.4706	0.5243	1.0621	1.1997	-0.5996	0.1790	0.4043	1.4703	1.6525
Naphthoquinones												
H	-0.1277	2.2260	1.5748	1.9650	2.0187	2.5566	2.6942	0.8948	1.6734	1.8987	2.9648	3.1469
2-NH_2	-0.1251	2.2960	1.6448	2.0350	2.0887	2.6265	2.7642	0.9648	1.7434	1.9687	3.0348	3.2169
2-OH	-0.1336	2.0636	1.4124	1.8026	1.8564	2.3942	2.5318	0.7324	1.5110	1.7363	2.8024	2.9845
2-CH_3	-0.1255	2.2862	1.6350	2.0252	2.0789	2.6167	2.7544	0.9550	1.7336	1.9589	3.0249	3.2071
2-CN	-0.1703	1.0665	0.4153	0.8055	0.8592	1.3971	1.5347	-0.2647	0.5139	0.7392	1.8053	1.9874
2-NO_2	-0.1606	1.3290	0.6778	1.0681	1.1218	1.6596	1.7972	-0.0022	0.7765	1.0017	2.0678	2.2500
5-NH_2	-0.1302	2.1580	1.5068	1.8970	1.9508	2.4886	2.6262	0.8268	1.6054	1.8307	2.8968	3.0790
5-OH	-0.1282	2.2111	1.5599	1.9501	2.0039	2.5417	2.6793	0.8799	1.6585	1.8838	2.9499	3.1320
5-CH_3	-0.1268	2.2504	1.5992	1.9894	2.0432	2.5810	2.7186	0.9192	1.6978	1.9231	2.9892	3.1713
5-CN	-0.1361	1.9974	1.3462	1.7365	1.7902	2.3280	2.4656	0.6662	1.4449	1.6701	2.7362	2.9184
5-NO_2	-0.1633	1.2578	0.6066	0.9969	1.0506	1.5884	1.7260	-0.0734	0.7053	0.9306	1.9966	2.1788
6-NH_2	-0.1242	2.3197	1.6685	2.0587	2.1124	2.6502	2.7879	0.9885	1.7671	1.9924	3.0584	3.2406
6-OH	-0.1291	2.1865	1.5353	1.9255	1.9792	2.5170	2.6547	0.8553	1.6339	1.8592	2.9252	3.1074
6-CH_3	-0.1274	2.2339	1.5827	1.9730	2.0267	2.5645	2.7021	0.9027	1.6814	1.9067	2.9727	3.1549
6-CN	-0.1376	1.9557	1.3045	1.6947	1.7484	2.2862	2.4239	0.6245	1.4031	1.6284	2.6945	2.8766
6-NO_2	-0.1493	1.6385	0.9873	1.3776	1.4313	1.9691	2.1067	0.3073	1.0860	1.3113	2.3773	2.5595
2,5,7-NH_2	-0.1052	2.8364	2.1852	2.5754	2.6291	3.1669	3.3046	1.5052	2.2838	2.5091	3.5751	3.7573
2,5,7-OH	-0.1191	2.4587	1.8075	2.1977	2.2514	2.7892	2.9269	1.1275	1.9061	2.1314	3.1974	3.3796
2,5,7-CH_3	-0.1171	2.5131	1.8619	2.2521	2.3059	2.8437	2.9813	1.1819	1.9605	2.1858	3.2519	3.4341
2,5,7-CN	-0.1588	1.3792	0.7280	1.1183	1.1720	1.7098	1.8474	0.0480	0.8267	1.0520	2.1180	2.3002
2,5,7-NO_2	-0.1619	1.2941	0.6429	1.0332	1.0869	1.6247	1.7623	-0.0371	0.7416	0.9669	2.0329	2.2151
2,5,8-NH_2	-0.1001	2.9759	2.3247	2.7149	2.7687	3.3065	3.4441	1.6447	2.4233	2.6486	3.7147	3.8969
2,5,8-OH	-0.1153	2.5623	1.9111	2.3014	2.3551	2.8929	3.0305	1.2311	2.0098	2.2350	3.3011	3.4833
2,5,8-CH_3	-0.1156	2.5546	1.9034	2.2936	2.3473	2.8852	3.0228	1.2234	2.0020	2.2273	3.2934	3.4755
2,5,8-CN	-0.1572	1.4219	0.7707	1.1610	1.2147	1.7525	1.8901	0.0908	0.8694	1.0947	2.1607	2.3429
2,5,8-NO_2	-0.1589	1.3770	0.7258	1.1160	1.1697	1.7076	1.8452	0.0458	0.8244	1.0497	2.1158	2.2979
2,6,8-NH_2	-0.0975	3.0478	2.3966	2.7869	2.8406	3.3784	3.5160	1.7166	2.4953	2.7206	3.7866	3.9688
2,6,8-OH	-0.1153	2.5615	1.9103	2.3005	2.3542	2.8920	3.0297	1.2303	2.0089	2.2342	3.3002	3.4824
2,6,8-CH_3	-0.1170	2.5161	1.8649	2.2552	2.3089	2.8467	2.9843	1.1849	1.9636	2.1889	3.2549	3.4371
2,6,8-CN	-0.1581	1.3981	0.7469	1.1372	1.1909	1.7287	1.8663	0.0669	0.8456	1.0709	2.1369	2.3191
2,6,8-NO_2	-0.1615	1.3054	0.6542	1.0445	1.0982	1.6360	1.7736	-0.0258	0.7529	0.9782	2.0442	2.2264
Anthraquinones												
H	-0.1183	2.4816	1.8304	2.2207	2.2744	2.8122	2.9498	1.1504	1.9291	2.1544	3.2204	3.4026
1-NH_2	-0.1214	2.3971	1.7459	2.1361	2.1899	2.7277	2.8653	1.0659	1.8445	2.0698	3.1359	3.3180
1-OH	-0.1192	2.4557	1.8045	2.1948	2.2485	2.7863	2.9239	1.1245	1.9032	2.1284	3.1945	3.3767
1-CH_3	-0.1565	1.4411	0.7899	1.1802	1.2339	1.7717	1.9093	0.1100	0.8886	1.1139	2.1799	2.3621
1-CN	-0.1299	2.1660	1.5148	1.9051	1.9588	2.4966	2.6342	0.8349	1.6135	1.8388	2.9048	3.0870
1-NO_2	-0.1539	1.5122	0.8610	1.2513	1.3050	1.8428	1.9804	0.1811	0.9597	1.1850	2.2510	2.4332
2-NH_2	-0.1144	2.5862	1.9350	2.3253	2.3790	2.9168	3.0544	1.2550	2.0337	2.2590	3.3250	3.5072
2-OH	-0.1173	2.5072	1.8560	2.2463	2.3000	2.8378	2.9754	1.1761	1.9547	2.1800	3.2460	3.4282
2-CH_3	-0.1293	2.1825	1.5313	1.9215	1.9753	2.5131	2.6507	0.8513	1.6299	1.8552	2.9213	3.1035
2-CN	-0.1419	1.8389	1.1877	1.5779	1.6317	2.1695	2.3071	0.5077	1.2863	1.5116	2.5777	2.7598
2-NO_2	-0.1193	2.4539	1.8027	2.1929	2.2466	2.7844	2.9221	1.1227	1.9013	2.1266	3.1927	3.3748
1,3,5,7-NH_2	-0.0910	3.2228	2.5716	2.9618	3.0155	3.5534	3.6910	1.8916	2.6702	2.8955	3.9616	4.1437
1,3,5,7-OH	-0.1013	2.9447	2.2935	2.6838	2.7375	3.2753	3.4129	1.6135	2.3922	2.6175	3.6835	3.8657
1,3,5,7-CH_3	-0.1069	2.7917	2.1405	2.5308	2.5845	3.1223	3.2599	1.4606	2.2392	2.4645	3.5305	3.7127
1,3,5,7-CN	-0.1487	1.6531	1.0019	1.3921	1.4459	1.9837	2.1213	0.3219	1.1005	1.3258	2.3919	2.5740
1,3,5,7-NO_2	-0.1555	1.4675	0.8163	1.2066	1.2603	1.7981	1.9357	0.1364	0.9150	1.1403	2.2063	2.3885

Table B.8: ΔE_1 (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	5-NH_2	5-OH	5-CH_3	5-CN	5-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.2032	0.1737	0.1834	0.1879	0.2071	0.2054	0.1687	0.1804	0.1862	0.2018	0.1811
Benzoquinones												
H	-0.1464	1.5465	0.7443	1.0087	1.1310	1.6526	1.6058	0.6085	0.9267	1.0849	1.5099	0.9449
2-NH_2	-0.1330	1.9089	1.1067	1.3711	1.4934	2.0150	1.9682	0.9709	1.2891	1.4473	1.8724	1.3073
2-OH	-0.1391	1.7440	0.9418	1.2062	1.3285	1.8501	1.8033	0.8060	1.1242	1.2824	1.7075	1.1424
2-CH_3	-0.1379	1.7762	0.9740	1.2384	1.3607	1.8823	1.8355	0.8382	1.1564	1.3146	1.7396	1.1745
2-CN	-0.1667	0.9921	0.1899	0.4543	0.5766	1.0982	1.0514	0.0541	0.3723	0.5305	0.9555	0.3904
2-NO_2	-0.1665	0.9982	0.1961	0.4604	0.5828	1.1043	1.0575	0.0603	0.3785	0.5367	0.9617	0.3966
2,5-NH_2	-0.1339	1.8847	1.0826	1.3469	1.4693	1.9909	1.9441	0.9468	1.2650	1.4232	1.8482	1.2831
2,5-OH	-0.1350	1.8546	1.0524	1.3168	1.4392	1.9607	1.9139	0.9166	1.2348	1.3931	1.8181	1.2530
2,5-CH_3	-0.1347	1.8633	1.0612	1.3255	1.4479	1.9695	1.9227	0.9254	1.2436	1.4018	1.8268	1.2617
2,5-CN	-0.1729	0.8244	0.0223	0.2866	0.4090	0.9306	0.8838	-0.1135	0.2047	0.3629	0.7879	0.2228
2,5-NO_2	-0.1826	0.5605	-0.2417	0.0227	0.1451	0.6666	0.6198	-0.3775	-0.0593	0.0990	0.5240	-0.0411
Naphthoquinones												
H	-0.1277	2.0549	1.2528	1.5171	1.6395	2.1611	2.1143	1.1170	1.4352	1.5934	2.0184	1.4533
2-NH_2	-0.1251	2.1249	1.3228	1.5871	1.7095	2.2311	2.1842	1.1870	1.5052	1.6634	2.0884	1.5233
2-OH	-0.1336	1.8925	1.0904	1.3547	1.4771	1.9987	1.9519	0.9546	1.2728	1.4310	1.8560	1.2909
2-CH_3	-0.1255	2.1151	1.3130	1.5773	1.6997	2.2212	2.1744	1.1772	1.4954	1.6536	2.0786	1.5135
2-CN	-0.1703	0.8954	0.0933	0.3576	0.4800	1.0016	0.9548	-0.0425	0.2757	0.4339	0.8589	0.2938
2-NO_2	-0.1606	1.1580	0.3558	0.6202	0.7425	1.2641	1.2173	0.2200	0.5382	0.6964	1.1214	0.5563
5-NH_2	-0.1302	1.9870	1.1848	1.4492	1.5715	2.0931	2.0463	1.0490	1.3672	1.5254	1.9504	1.3853
5-OH	-0.1282	2.0400	1.2379	1.5023	1.6246	2.1462	2.0994	1.1021	1.4203	1.5785	2.0035	1.4384
5-CH_3	-0.1268	2.0793	1.2772	1.5415	1.6639	2.1855	2.1387	1.1414	1.4596	1.6178	2.0428	1.4777
5-CN	-0.1361	1.8264	1.0242	1.2886	1.4109	1.9325	1.8857	0.8884	1.2066	1.3648	1.7898	1.2247
5-NO_2	-0.1633	1.0868	0.2846	0.5490	0.6713	1.1929	1.1461	0.1488	0.4670	0.6252	1.0502	0.4852
6-NH_2	-0.1242	2.1486	1.3465	1.6108	1.7332	2.2547	2.2079	1.2107	1.5289	1.6871	2.1121	1.5470
6-OH	-0.1291	2.0154	1.2132	1.4776	1.6000	2.1215	2.0747	1.0775	1.3956	1.5539	1.9789	1.4138
6-CH_3	-0.1274	2.0629	1.2607	1.5251	1.6474	2.1690	2.1222	1.1249	1.4431	1.6013	2.0263	1.4613
6-CN	-0.1376	1.7846	0.9825	1.2468	1.3692	1.8907	1.8439	0.8467	1.1649	1.3231	1.7481	1.1830
6-NO_2	-0.1493	1.4675	0.6653	0.9297	1.0520	1.5736	1.5268	0.5295	0.8477	1.0059	1.4309	0.8658
2,5,7-NH_2	-0.1052	2.6653	1.8632	2.1275	2.2499	2.7714	2.7246	1.7274	2.0456	2.2038	2.6288	2.0637
2,5,7-OH	-0.1191	2.2876	1.4855	1.7498	1.8722	2.3937	2.3469	1.3497	1.6679	1.8261	2.2511	1.6860
2,5,7-CH_3	-0.1171	2.3421	1.5399	1.8043	1.9266	2.4482	2.4014	1.4041	1.7223	1.8805	2.3055	1.7404
2,5,7-CN	-0.1588	1.2082	0.4060	0.6704	0.7927	1.3143	1.2675	0.2702	0.5884	0.7466	1.1716	0.6066
2,5,7-NO_2	-0.1619	1.1231	0.3209	0.5853	0.7076	1.2292	1.1824	0.1851	0.5033	0.6615	1.0866	0.5215
2,5,8-NH_2	-0.1001	2.8049	2.0027	2.2671	2.3894	2.9110	2.8642	1.8669	2.1851	2.3433	2.7683	2.2032
2,5,8-OH	-0.1153	2.3913	1.5891	1.8535	1.9758	2.4974	2.4506	1.4533	1.7715	1.9297	2.3547	1.7896
2,5,8-CH_3	-0.1156	2.3835	1.5814	1.8457	1.9681	2.4897	2.4429	1.4456	1.7638	1.9220	2.3470	1.7819
2,5,8-CN	-0.1572	1.2509	0.4487	0.7131	0.8354	1.3570	1.3102	0.3129	0.6311	0.7893	1.2144	0.6493
2,5,8-NO_2	-0.1589	1.2059	0.4038	0.6681	0.7905	1.3121	1.2653	0.2680	0.5862	0.7444	1.1694	0.6043
2,6,8-NH_2	-0.0975	2.8768	2.0746	2.3390	2.4613	2.9829	2.9361	1.9388	2.2570	2.4152	2.8403	2.2752
2,6,8-OH	-0.1153	2.3904	1.5882	1.8526	1.9750	2.4965	2.4497	1.4525	1.7706	1.9289	2.3539	1.7888
2,6,8-CH_3	-0.1170	2.3451	1.5429	1.8073	1.9296	2.4512	2.4044	1.4071	1.7253	1.8835	2.3085	1.7434
2,6,8-CN	-0.1581	1.2271	0.4249	0.6893	0.8116	1.3332	1.2864	0.2891	0.6073	0.7655	1.1906	0.6255
2,6,8-NO_2	-0.1615	1.1344	0.3322	0.5966	0.7189	1.2405	1.1937	0.1964	0.5146	0.6728	1.0978	0.5328
Anthraquinones												
H	-0.1183	2.3106	1.5084	1.7728	1.8951	2.4167	2.3699	1.3726	1.6908	1.8490	2.2741	1.7090
1-NH_2	-0.1214	2.2260	1.4239	1.6882	1.8106	2.3322	2.2854	1.2881	1.6063	1.7645	2.1895	1.6244
1-OH	-0.1192	2.2847	1.4825	1.7469	1.8692	2.3908	2.3440	1.3467	1.6649	1.8231	2.2481	1.6830
1-CH_3	-0.1565	1.2701	0.4679	0.7323	0.8547	1.3762	1.3294	0.3321	0.6503	0.8086	1.2336	0.6685
1-CN	-0.1299	1.9950	1.1928	1.4572	1.5795	2.1011	2.0543	1.0570	1.3752	1.5334	1.9585	1.3934
1-NO_2	-0.1539	1.3412	0.5390	0.8034	0.9257	1.4473	1.4005	0.4032	0.7214	0.8796	1.3047	0.7396
2-NH_2	-0.1144	2.4152	1.6130	1.8774	1.9997	2.5213	2.4745	1.4772	1.7954	1.9536	2.3787	1.8136
2-OH	-0.1173	2.3362	1.5340	1.7984	1.9207	2.4423	2.3955	1.3982	1.7164	1.8747	2.2997	1.7346
2-CH_3	-0.1293	2.0115	1.2093	1.4737	1.5960	2.1176	2.0708	1.0735	1.3917	1.5499	1.9749	1.4098
2-CN	-0.1419	1.6678	0.8657	1.1300	1.2524	1.7740	1.7272	0.7299	1.0481	1.2063	1.6313	1.0662
2-NO_2	-0.1193	2.2828	1.4807	1.7450	1.8674	2.3890	2.3422	1.3449	1.6631	1.8213	2.2463	1.6812
1,3,5,7-NH_2	-0.0910	3.0517	2.2496	2.5139	2.6363	3.1579	3.1111	2.1138	2.4320	2.5902	3.0152	2.4501
1,3,5,7-OH	-0.1013	2.7737	1.9715	2.2359	2.3582	2.8798	2.8330	1.8357	2.1539	2.3121	2.7372	2.1721
1,3,5,7-CH_3	-0.1069	2.6207	1.8185	2.0829	2.2052	2.7268	2.6800	1.6827	2.0009	2.1591	2.5842	2.0191
1,3,5,7-CN	-0.1487	1.4820	0.6799	0.9443	1.0666	1.5882	1.5414	0.5441	0.8623	1.0205	1.4455	0.8804
1,3,5,7-NO_2	-0.1555	1.2965	0.4943	0.7587	0.8810	1.4026	1.3558	0.3585	0.6767	0.8349	1.2600	0.6949

Table B.9: ΔE_1 (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	6-NH_2	6-OH	6-CH_3	6-CN	6-NO_2	2,5,7-NH_2	2,5,7-OH	2,5,7-CH_3	2,5,7-CN	2,5,7-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.1755	0.1857	0.1886	0.2033	0.1985	0.1705	0.1928	0.1944	0.2388	0.2466
Benzoquinones											
H	-0.1464	0.7922	1.0702	1.1507	1.5498	1.4176	0.6564	1.2639	1.3068	2.5158	2.7273
2-NH_2	-0.1330	1.1546	1.4326	1.5131	1.9122	1.7800	1.0188	1.6263	1.6692	2.8782	3.0897
2-OH	-0.1391	0.9897	1.2677	1.3482	1.7473	1.6151	0.8539	1.4614	1.5043	2.7133	2.9248
2-CH_3	-0.1379	1.0219	1.2999	1.3804	1.7794	1.6473	0.8861	1.4935	1.5365	2.7455	2.9569
2-CN	-0.1667	0.2378	0.5158	0.5963	0.9953	0.8632	0.1020	0.7094	0.7524	1.9613	2.1728
2-NO_2	-0.1665	0.2440	0.5220	0.6024	1.0015	0.8694	0.1082	0.7156	0.7586	1.9675	2.1790
2,5-NH_2	-0.1339	1.1305	1.4085	1.4890	1.8880	1.7559	0.9947	1.6021	1.6451	2.8540	3.0655
2,5-OH	-0.1350	1.1004	1.3784	1.4588	1.8579	1.7257	0.9646	1.5720	1.6150	2.8239	3.0354
2,5-CH_3	-0.1347	1.1091	1.3871	1.4676	1.8666	1.7345	0.9733	1.5807	1.6237	2.8326	3.0441
2,5-CN	-0.1729	0.0702	0.3482	0.4287	0.8277	0.6956	-0.0656	0.5418	0.5848	1.7937	2.0052
2,5-NO_2	-0.1826	-0.1937	0.0843	0.1647	0.5638	0.4316	-0.3295	0.2779	0.3209	1.5298	1.7413
Naphthoquinones											
H	-0.1277	1.3007	1.5787	1.6592	2.0582	1.9261	1.1649	1.7723	1.8153	3.0242	3.2357
2-NH_2	-0.1251	1.3707	1.6487	1.7292	2.1282	1.9961	1.2349	1.8423	1.8853	3.0942	3.3057
2-OH	-0.1336	1.1383	1.4163	1.4968	1.8958	1.7637	1.0025	1.6099	1.6529	2.8618	3.0733
2-CH_3	-0.1255	1.3609	1.6389	1.7193	2.1184	1.9863	1.2251	1.8325	1.8755	3.0844	3.2959
2-CN	-0.1703	0.1412	0.4192	0.4997	0.8987	0.7666	0.0054	0.6128	0.6558	1.8647	2.0762
2-NO_2	-0.1606	0.4037	0.6817	0.7622	1.1612	1.0291	0.2679	0.8753	0.9183	2.1273	2.3387
5-NH_2	-0.1302	1.2327	1.5107	1.5912	1.9902	1.8581	1.0969	1.7043	1.7473	2.9563	3.1677
5-OH	-0.1282	1.2858	1.5638	1.6443	2.0433	1.9112	1.1500	1.7574	1.8004	3.0093	3.2208
5-CH_3	-0.1268	1.3251	1.6031	1.6836	2.0826	1.9505	1.1893	1.7967	1.8397	3.0486	3.2601
5-CN	-0.1361	1.0721	1.3501	1.4306	1.8296	1.6975	0.9363	1.5437	1.5867	2.7957	3.0071
5-NO_2	-0.1633	0.3325	0.6105	0.6910	1.0901	0.9579	0.1967	0.8042	0.8471	2.0561	2.2676
6-NH_2	-0.1242	1.3944	1.6724	1.7528	2.1519	2.0198	1.2586	1.8660	1.9090	3.1179	3.3294
6-OH	-0.1291	1.2612	1.5392	1.6196	2.0187	1.8865	1.1254	1.7328	1.7758	2.9847	3.1962
6-CH_3	-0.1274	1.3086	1.5866	1.6671	2.0662	1.9340	1.1728	1.7803	1.8232	3.0322	3.2437
6-CN	-0.1376	1.0304	1.3084	1.3888	1.7879	1.6558	0.8946	1.5020	1.5450	2.7539	2.9654
6-NO_2	-0.1493	0.7132	0.9912	1.0717	1.4708	1.3386	0.5774	1.1849	1.2278	2.4368	2.6483
2,5,7-NH_2	-0.1052	1.9111	2.1891	2.2695	2.6686	2.5365	1.7753	2.3827	2.4257	3.6346	3.8461
2,5,7-OH	-0.1191	1.5334	1.8114	1.8918	2.2909	2.1588	1.3976	2.0050	2.0480	3.2569	3.4684
2,5,7-CH_3	-0.1171	1.5878	1.8658	1.9463	2.3453	2.2132	1.4520	2.0594	2.1024	3.3113	3.5228
2,5,7-CN	-0.1588	0.4539	0.7319	0.8124	1.2115	1.0793	0.3181	0.9256	0.9685	2.1775	2.3890
2,5,7-NO_2	-0.1619	0.3688	0.6468	0.7273	1.1264	0.9942	0.2330	0.8405	0.8834	2.0924	2.3039
2,5,8-NH_2	-0.1001	2.0506	2.3286	2.4091	2.8081	2.6760	1.9148	2.5222	2.5652	3.7741	3.9856
2,5,8-OH	-0.1153	1.6370	1.9150	1.9955	2.3945	2.2624	1.5012	2.1086	2.1516	3.3606	3.5720
2,5,8-CH_3	-0.1156	1.6293	1.9073	1.9878	2.3868	2.2547	1.4935	2.1009	2.1439	3.3528	3.5643
2,5,8-CN	-0.1572	0.4966	0.7746	0.8551	1.2542	1.1220	0.3608	0.9683	1.0112	2.2202	2.4317
2,5,8-NO_2	-0.1589	0.4517	0.7297	0.8102	1.2092	1.0771	0.3159	0.9233	0.9663	2.1752	2.3867
2,6,8-NH_2	-0.0975	2.1225	2.4005	2.4810	2.8801	2.7479	1.9867	2.5942	2.6371	3.8461	4.0576
2,6,8-OH	-0.1153	1.6362	1.9142	1.9946	2.3937	2.2615	1.5004	2.1078	2.1508	3.3597	3.5712
2,6,8-CH_3	-0.1170	1.5908	1.8688	1.9493	2.3483	2.2162	1.4550	2.0624	2.1054	3.3144	3.5258
2,6,8-CN	-0.1581	0.4728	0.7508	0.8313	1.2304	1.0982	0.3370	0.9445	0.9874	2.1964	2.4079
2,6,8-NO_2	-0.1615	0.3801	0.6581	0.7386	1.1377	1.0055	0.2443	0.8518	0.8947	2.1037	2.3152
Anthraquinones											
H	-0.1183	1.5563	1.8343	1.9148	2.3139	2.1817	1.4205	2.0280	2.0709	3.2799	3.4914
1-NH_2	-0.1214	1.4718	1.7498	1.8303	2.2293	2.0972	1.3360	1.9434	1.9864	3.1953	3.4068
1-OH	-0.1192	1.5304	1.8084	1.8889	2.2879	2.1558	1.3946	2.0020	2.0450	3.2540	3.4654
1-CH_3	-0.1565	0.5159	0.7939	0.8743	1.2734	1.1412	0.3801	0.9875	1.0305	2.2394	2.4509
1-CN	-0.1299	1.2408	1.5187	1.5992	1.9983	1.8661	1.1049	1.7124	1.7553	2.9643	3.1758
1-NO_2	-0.1539	0.5870	0.8649	0.9454	1.3445	1.2123	0.4512	1.0586	1.1015	2.3105	2.5220
2-NH_2	-0.1144	1.6609	1.9389	2.0194	2.4185	2.2863	1.5251	2.1326	2.1755	3.3845	3.5960
2-OH	-0.1173	1.5820	1.8599	1.9404	2.3395	2.2073	1.4462	2.0536	2.0965	3.3055	3.5170
2-CH_3	-0.1293	1.2572	1.5352	1.6157	2.0147	1.8826	1.1214	1.7288	1.7718	2.9807	3.1922
2-CN	-0.1419	0.9136	1.1916	1.2721	1.6711	1.5390	0.7778	1.3852	1.4282	2.6371	2.8486
2-NO_2	-0.1193	1.5286	1.8066	1.8871	2.2861	2.1540	1.3928	2.0002	2.0432	3.2521	3.4636
1,3,5,7-NH_2	-0.0910	2.2975	2.5755	2.6560	3.0550	2.9229	2.1617	2.7691	2.8121	4.0210	4.2325
1,3,5,7-OH	-0.1013	2.0194	2.2974	2.3779	2.7770	2.6448	1.8836	2.4911	2.5340	3.7430	3.9545
1,3,5,7-CH_3	-0.1069	1.8665	2.1444	2.2249	2.6240	2.4918	1.7307	2.3381	2.3810	3.5900	3.8015
1,3,5,7-CN	-0.1487	0.7278	1.0058	1.0863	1.4853	1.3532	0.5920	1.1994	1.2424	2.4513	2.6628
1,3,5,7-NO_2	-0.1555	0.5423	0.8202	0.9007	1.2998	1.1676	0.4065	1.0139	1.0568	2.2658	2.4773

Table B.10: ΔE_1 (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	2,5,8-NH_2	2,5,8-OH	2,5,8-CH_3	2,5,8-CN	2,5,8-NO_2	2,6,8-NH_2	2,6,8-OH	2,6,8-CH_3	2,6,8-CN	2,6,8-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.1686	0.1854	0.1917	0.2382	0.2439	0.1629	0.1895	0.1937	0.2387	0.2451
Benzoquinones											
H	-0.1464	0.6046	1.0633	1.2326	2.4987	2.6551	0.4511	1.1749	1.2872	2.5128	2.6860
2-NH_2	-0.1330	0.9670	1.4258	1.5950	2.8611	3.0176	0.8135	1.5373	1.6496	2.8752	3.0484
2-OH	-0.1391	0.8021	1.2609	1.4301	2.6962	2.8526	0.6486	1.3724	1.4847	2.7103	2.8835
2-CH_3	-0.1379	0.8342	1.2930	1.4623	2.7283	2.8848	0.6808	1.4046	1.5169	2.7425	2.9157
2-CN	-0.1667	0.0501	0.5089	0.6782	1.9442	2.1007	-0.1034	0.6205	0.7328	1.9584	2.1316
2-NO_2	-0.1665	0.0563	0.5151	0.6843	1.9504	2.1069	-0.0972	0.6267	0.7389	1.9645	2.1378
2,5-NH_2	-0.1339	0.9428	1.4016	1.5708	2.8369	2.9934	0.7893	1.5132	1.6254	2.8511	3.0243
2,5-OH	-0.1350	0.9127	1.3715	1.5407	2.8068	2.9633	0.7592	1.4830	1.5953	2.8209	2.9942
2,5-CH_3	-0.1347	0.9214	1.3802	1.5494	2.8155	2.9720	0.7679	1.4918	1.6040	2.8297	3.0029
2,5-CN	-0.1729	-0.1175	0.3413	0.5105	1.7766	1.9331	-0.2710	0.4529	0.5651	1.7908	1.9640
2,5-NO_2	-0.1826	-0.3814	0.0774	0.2466	1.5127	1.6692	-0.5349	0.1889	0.3012	1.5268	1.7001
Naphthoquinones											
H	-0.1277	1.1130	1.5718	1.7410	3.0071	3.1636	0.9595	1.6834	1.7956	3.0213	3.1945
2-NH_2	-0.1251	1.1830	1.6418	1.8110	3.0771	3.2336	1.0295	1.7534	1.8656	3.0913	3.2645
2-OH	-0.1336	0.9506	1.4094	1.5786	2.8447	3.0012	0.7971	1.5210	1.6332	2.8589	3.0321
2-CH_3	-0.1255	1.1732	1.6320	1.8012	3.0673	3.2238	1.0197	1.7436	1.8558	3.0814	3.2547
2-CN	-0.1703	-0.0465	0.4123	0.5815	1.8476	2.0041	-0.2000	0.5239	0.6361	1.8618	2.0350
2-NO_2	-0.1606	0.2160	0.6748	0.8441	2.1101	2.2666	0.0626	0.7864	0.8987	2.1243	2.2975
5-NH_2	-0.1302	1.0450	1.5038	1.6731	2.9391	3.0956	0.8916	1.6154	1.7277	2.9533	3.1265
5-OH	-0.1282	1.0981	1.5569	1.7262	2.9922	3.1487	0.9446	1.6685	1.7808	3.0064	3.1796
5-CH_3	-0.1268	1.1374	1.5962	1.7654	3.0315	3.1880	0.9839	1.7078	1.8200	3.0457	3.2189
5-CN	-0.1361	0.8844	1.3432	1.5125	2.7785	2.9350	0.7310	1.4548	1.5671	2.7927	2.9659
5-NO_2	-0.1633	0.1449	0.6037	0.7729	2.0390	2.1954	-0.0086	0.7152	0.8275	2.0531	2.2263
6-NH_2	-0.1242	1.2067	1.6655	1.8347	3.1008	3.2573	1.0532	1.7771	1.8893	3.1149	3.2882
6-OH	-0.1291	1.0735	1.5323	1.7015	2.9676	3.1241	0.9200	1.6438	1.7561	2.9817	3.1550
6-CH_3	-0.1274	1.1210	1.5797	1.7490	3.0151	3.1715	0.9675	1.6913	1.8036	3.0292	3.2024
6-CN	-0.1376	0.8427	1.3015	1.4707	2.7368	2.8933	0.6892	1.4131	1.5253	2.7509	2.9242
6-NO_2	-0.1493	0.5256	0.9843	1.1536	2.4197	2.5761	0.3721	1.0959	1.2082	2.4338	2.6070
2,5,7-NH_2	-0.1052	1.7234	2.1822	2.3514	3.6175	3.7740	1.5699	2.2938	2.4060	3.6316	3.8049
2,5,7-OH	-0.1191	1.3457	1.8045	1.9737	3.2398	3.3963	1.1922	1.9161	2.0283	3.2539	3.4272
2,5,7-CH_3	-0.1171	1.4001	1.8589	2.0282	3.2942	3.4507	1.2466	1.9705	2.0828	3.3084	3.4816
2,5,7-CN	-0.1588	0.2663	0.7250	0.8943	2.1604	2.3168	0.1128	0.8366	0.9489	2.1745	2.3477
2,5,7-NO_2	-0.1619	0.1812	0.6400	0.8092	2.0753	2.2318	0.0277	0.7515	0.8638	2.0894	2.2626
2,5,8-NH_2	-0.1001	1.8629	2.3217	2.4910	3.7570	3.9135	1.7094	2.4333	2.5456	3.7712	3.9444
2,5,8-OH	-0.1153	1.4493	1.9081	2.0774	3.3434	3.4999	1.2959	2.0197	2.1320	3.3576	3.5308
2,5,8-CH_3	-0.1156	1.4416	1.9004	2.0696	3.3357	3.4922	1.2881	2.0120	2.1242	3.3499	3.5231
2,5,8-CN	-0.1572	0.3090	0.7678	0.9370	2.2031	2.3596	0.1555	0.8793	0.9916	2.2172	2.3904
2,5,8-NO_2	-0.1589	0.2640	0.7228	0.8920	2.1581	2.3146	0.1105	0.8344	0.9466	2.1723	2.3455
2,6,8-NH_2	-0.0975	1.9349	2.3937	2.5629	3.8290	3.9855	1.7814	2.5052	2.6175	3.8431	4.0163
2,6,8-OH	-0.1153	1.4485	1.9073	2.0765	3.3426	3.4991	1.2950	2.0188	2.1311	3.3567	3.5300
2,6,8-CH_3	-0.1170	1.4031	1.8619	2.0312	3.2973	3.4537	1.2497	1.9735	2.0858	3.3114	3.4846
2,6,8-CN	-0.1581	0.2852	0.7440	0.9132	2.1793	2.3358	0.1317	0.8555	0.9678	2.1934	2.3666
2,6,8-NO_2	-0.1615	0.1925	0.6512	0.8205	2.0866	2.2430	0.0390	0.7628	0.8751	2.1007	2.2739
Anthraquinones											
H	-0.1183	1.3687	1.8275	1.9967	3.2628	3.4193	1.2152	1.9390	2.0513	3.2769	3.4501
1-NH_2	-0.1214	1.2841	1.7429	1.9121	3.1782	3.3347	1.1306	1.8545	1.9667	3.1924	3.3656
1-OH	-0.1192	1.3427	1.8015	1.9708	3.2368	3.3933	1.1893	1.9131	2.0254	3.2510	3.4242
1-CH_3	-0.1565	0.3282	0.7870	0.9562	2.2223	2.3788	0.1747	0.8985	1.0108	2.2364	2.4097
1-CN	-0.1299	1.0531	1.5119	1.6811	2.9472	3.1037	0.8996	1.6234	1.7357	2.9613	3.1346
1-NO_2	-0.1539	0.3993	0.8581	1.0273	2.2934	2.4499	0.2458	0.9696	1.0819	2.3075	2.4808
2-NH_2	-0.1144	1.4733	1.9321	2.1013	3.3674	3.5239	1.3198	2.0436	2.1559	3.3815	3.5547
2-OH	-0.1173	1.3943	1.8531	2.0223	3.2884	3.4449	1.2408	1.9646	2.0769	3.3025	3.4758
2-CH_3	-0.1293	1.0695	1.5283	1.6976	2.9636	3.1201	0.9160	1.6399	1.7522	2.9778	3.1510
2-CN	-0.1419	0.7259	1.1847	1.3539	2.6200	2.7765	0.5724	1.2963	1.4085	2.6342	2.8074
2-NO_2	-0.1193	1.3409	1.7997	1.9689	3.2350	3.3915	1.1874	1.9113	2.0235	3.2492	3.4224
1,3,5,7-NH_2	-0.0910	2.1098	2.5686	2.7378	4.0039	4.1604	1.9563	2.6802	2.7924	4.0181	4.1913
1,3,5,7-OH	-0.1013	1.8318	2.2906	2.4598	3.7259	3.8824	1.6783	2.4021	2.5144	3.7400	3.9132
1,3,5,7-CH_3	-0.1069	1.6788	2.1376	2.3068	3.5729	3.7294	1.5253	2.2491	2.3614	3.5870	3.7603
1,3,5,7-CN	-0.1487	0.5401	0.9989	1.1681	2.4342	2.5907	0.3866	1.1105	1.2228	2.4484	2.6216
1,3,5,7-NO_2	-0.1555	0.3546	0.8134	0.9826	2.2487	2.4052	0.2011	0.9249	1.0372	2.2628	2.4361

Table B.11: ΔE_1 (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised AH_2Q	H	1-NH_2	1-OH	1-CH_3	1-CN	1-NO_2	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	0.1869	0.1539	0.1621	0.1668	0.1860	0.1615	0.1592	0.1670	0.1697	0.1854	0.1797
Benzoquinones												
H	-0.1464	1.1033	0.2060	0.4285	0.5572	1.0775	0.4121	0.3506	0.5619	0.6343	1.0612	0.9064
2-NH_2	-0.1330	1.4657	0.5684	0.7909	0.9196	1.4399	0.7745	0.7130	0.9243	0.9967	1.4236	1.2688
2-OH	-0.1391	1.3008	0.4035	0.6260	0.7547	1.2750	0.6096	0.5481	0.7594	0.8318	1.2587	1.1039
2-CH_3	-0.1379	1.3330	0.4357	0.6582	0.7869	1.3072	0.6418	0.5803	0.7915	0.8640	1.2909	1.1361
2-CN	-0.1667	0.5488	-0.3484	-0.1259	0.0028	0.5230	-0.1423	-0.2038	0.0074	0.0799	0.5068	0.3520
2-NO_2	-0.1665	0.5550	-0.3422	-0.1197	0.0090	0.5292	-0.1361	-0.1977	0.0136	0.0860	0.5130	0.3582
2,5-NH_2	-0.1339	1.4415	0.5443	0.7668	0.8955	1.4157	0.7504	0.6889	0.9001	0.9726	1.3995	1.2447
2,5-OH	-0.1350	1.4114	0.5142	0.7366	0.8654	1.3856	0.7203	0.6587	0.8700	0.9424	1.3693	1.2146
2,5-CH_3	-0.1347	1.4201	0.5229	0.7454	0.8741	1.3943	0.7290	0.6675	0.8787	0.9512	1.3781	1.2233
2,5-CN	-0.1729	0.3812	-0.5160	-0.2935	-0.1648	0.3554	-0.3099	-0.3714	-0.1602	-0.0877	0.3392	0.1844
2,5-NO_2	-0.1826	0.1173	-0.7799	-0.5575	-0.4287	0.0915	-0.5738	-0.6354	-0.4241	-0.3517	0.0752	-0.0795
Naphthoquinones												
H	-0.1277	1.6117	0.7145	0.9370	1.0657	1.5859	0.9206	0.8591	1.0703	1.1428	1.5697	1.4149
2-NH_2	-0.1251	1.6817	0.7845	1.0070	1.1357	1.6559	0.9906	0.9290	1.1403	1.2127	1.6397	1.4849
2-OH	-0.1336	1.4493	0.5521	0.7746	0.9033	1.4235	0.7582	0.6967	0.9079	0.9804	1.4073	1.2525
2-CH_3	-0.1255	1.6719	0.7747	0.9972	1.1259	1.6461	0.9808	0.9192	1.1305	1.2029	1.6299	1.4751
2-CN	-0.1703	0.4522	-0.4450	-0.2225	-0.0938	0.4264	-0.2389	-0.3005	-0.0892	-0.0167	0.4102	0.2554
2-NO_2	-0.1606	0.7148	-0.1825	0.0400	0.1687	0.6890	0.0236	-0.0379	0.1733	0.2458	0.6727	0.5179
5-NH_2	-0.1302	1.5438	0.6465	0.8690	0.9977	1.5180	0.8526	0.7911	1.0023	1.0748	1.5017	1.3469
5-OH	-0.1282	1.5968	0.6996	0.9221	1.0508	1.5710	0.9057	0.8442	1.0554	1.1279	1.5548	1.4000
5-CH_3	-0.1268	1.6361	0.7389	0.9614	1.0901	1.6103	0.9450	0.8835	1.0947	1.1672	1.5941	1.4393
5-CN	-0.1361	1.3832	0.4859	0.7084	0.8371	1.3574	0.6920	0.6305	0.8417	0.9142	1.3411	1.1863
5-NO_2	-0.1633	0.6436	-0.2537	-0.0312	0.0975	0.6178	-0.0476	-0.1091	0.1022	0.1746	0.6015	0.4467
6-NH_2	-0.1242	1.7054	0.8082	1.0307	1.1594	1.6796	1.0143	0.9527	1.1640	1.2364	1.6634	1.5086
6-OH	-0.1291	1.5722	0.6750	0.8975	1.0262	1.5464	0.8811	0.8195	1.0308	1.1032	1.5302	1.3754
6-CH_3	-0.1274	1.6197	0.7224	0.9449	1.0736	1.5939	0.9285	0.8670	1.0783	1.1507	1.5776	1.4228
6-CN	-0.1376	1.3414	0.4442	0.6667	0.7954	1.3156	0.6503	0.5887	0.8000	0.8724	1.2994	1.1446
6-NO_2	-0.1493	1.0243	0.1270	0.3495	0.4782	0.9985	0.3331	0.2716	0.4829	0.5553	0.9822	0.8274
2,5,7-NH_2	-0.1052	2.2221	1.3249	1.5474	1.6761	2.1963	1.5310	1.4694	1.6807	1.7531	2.1801	2.0253
2,5,7-OH	-0.1191	1.8444	0.9472	1.1697	1.2984	1.8186	1.1533	1.0917	1.3030	1.3754	1.8024	1.6476
2,5,7-CH_3	-0.1171	1.8988	1.0016	1.2241	1.3528	1.8731	1.2077	1.1462	1.3574	1.4299	1.8568	1.7020
2,5,7-CN	-0.1588	0.7650	-0.1323	0.0902	0.2189	0.7392	0.0738	0.0123	0.2236	0.2960	0.7229	0.5681
2,5,7-NO_2	-0.1619	0.6799	-0.2174	0.0051	0.1338	0.6541	-0.0113	-0.0728	0.1385	0.2109	0.6378	0.4830
2,5,8-NH_2	-0.1001	2.3616	1.4644	1.6869	1.8156	2.3358	1.6705	1.6090	1.8202	1.8927	2.3196	2.1648
2,5,8-OH	-0.1153	1.9481	1.0508	1.2733	1.4020	1.9223	1.2569	1.1954	1.4066	1.4791	1.9060	1.7512
2,5,8-CH_3	-0.1156	1.9403	1.0431	1.2656	1.3943	1.9145	1.2492	1.1876	1.3989	1.4714	1.8983	1.7435
2,5,8-CN	-0.1572	0.8077	-0.0895	0.1329	0.2616	0.7819	0.1165	0.0550	0.2663	0.3387	0.7656	0.6108
2,5,8-NO_2	-0.1589	0.7627	-0.1345	0.0880	0.2167	0.7369	0.0716	0.0101	0.2213	0.2938	0.7207	0.5659
2,6,8-NH_2	-0.0975	2.4336	1.5363	1.7588	1.8875	2.4078	1.7424	1.6809	1.8922	1.9646	2.3915	2.2367
2,6,8-OH	-0.1153	1.9472	1.0500	1.2725	1.4012	1.9214	1.2561	1.1945	1.4058	1.4782	1.9052	1.7504
2,6,8-CH_3	-0.1170	1.9019	1.0046	1.2271	1.3558	1.8761	1.2107	1.1492	1.3604	1.4329	1.8598	1.7050
2,6,8-CN	-0.1581	0.7839	-0.1134	0.1091	0.2378	0.7581	0.0927	0.0312	0.2425	0.3149	0.7418	0.5870
2,6,8-NO_2	-0.1615	0.6912	-0.2061	0.0164	0.1451	0.6654	0.0000	-0.0615	0.1498	0.2222	0.6491	0.4943
Anthraquinones												
H	-0.1183	1.8674	0.9701	1.1926	1.3213	1.8416	1.1762	1.1147	1.3260	1.3984	1.8253	1.6705
1-NH_2	-0.1214	1.7828	0.8856	1.1081	1.2368	1.7570	1.0917	1.0302	1.2414	1.3139	1.7408	1.5860
1-OH	-0.1192	1.8415	0.9442	1.1667	1.2954	1.8157	1.1503	1.0888	1.3000	1.3725	1.7994	1.6446
1-CH_3	-0.1565	0.8269	-0.0703	0.1521	0.2809	0.8011	0.1358	0.0742	0.2855	0.3579	0.7848	0.6301
1-CN	-0.1299	1.5518	0.6546	0.8770	1.0057	1.5260	0.8607	0.7991	1.0104	1.0828	1.5097	1.3549
1-NO_2	-0.1539	0.8980	0.0008	0.2232	0.3519	0.8722	0.2069	0.1453	0.3566	0.4290	0.8559	0.7011
2-NH_2	-0.1144	1.9720	1.0748	1.2972	1.4259	1.9462	1.2808	1.2193	1.4306	1.5030	1.9299	1.7751
2-OH	-0.1173	1.8930	0.9958	1.2182	1.3469	1.8672	1.2019	1.1403	1.3516	1.4240	1.8509	1.6961
2-CH_3	-0.1293	1.5682	0.6710	0.8935	1.0222	1.5424	0.8771	0.8156	1.0268	1.0993	1.5262	1.3714
2-CN	-0.1419	1.2246	0.3274	0.5499	0.6786	1.1988	0.5335	0.4720	0.6832	0.7557	1.1826	1.0278
2-NO_2	-0.1193	1.8396	0.9424	1.1649	1.2936	1.8138	1.1485	1.0869	1.2982	1.3706	1.7976	1.6428
1,3,5,7-NH_2	-0.0910	2.6085	1.7113	1.9338	2.0625	2.5827	1.9174	1.8559	2.0671	2.1396	2.5665	2.4117
1,3,5,7-OH	-0.1013	2.3305	1.4332	1.6557	1.7844	2.3047	1.6393	1.5778	1.7891	1.8615	2.2884	2.1336
1,3,5,7-CH_3	-0.1069	2.1775	1.2803	1.5027	1.6314	2.1517	1.4864	1.4248	1.6361	1.7085	2.1354	1.9806
1,3,5,7-CN	-0.1487	1.0388	0.1416	0.3641	0.4928	1.0130	0.3477	0.2862	0.4974	0.5699	0.9968	0.8420
1,3,5,7-NO_2	-0.1555	0.8533	-0.0439	0.1785	0.3072	0.8275	0.1622	0.1006	0.3119	0.3843	0.8112	0.6564

Table B.12: ΔE_1 (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised AH_2Q	1,3,5,7-NH_2	1,3,5,7-OH	1,3,5,7-CH_3	1,3,5,7-CN	1,3,5,7-NO_2
Reduced quinone	$\Delta E_{\text{absolute}}$ (E_h)	0.1541	0.1765	0.1778	0.2312	0.2331
Benzoquinones						
H	-0.1464	0.2098	0.8199	0.8568	2.3073	2.3617
2-NH_2	-0.1330	0.5722	1.1823	1.2192	2.6697	2.7241
2-OH	-0.1391	0.4073	1.0174	1.0543	2.5048	2.5592
2-CH_3	-0.1379	0.4394	1.0496	1.0864	2.5370	2.5914
2-CN	-0.1667	-0.3447	0.2654	0.3023	1.7529	1.8073
2-NO_2	-0.1665	-0.3385	0.2716	0.3085	1.7591	1.8134
2,5-NH_2	-0.1339	0.5480	1.1581	1.1950	2.6456	2.7000
2,5-OH	-0.1350	0.5179	1.1280	1.1649	2.6155	2.6698
2,5-CH_3	-0.1347	0.5266	1.1367	1.1736	2.6242	2.6786
2,5-CN	-0.1729	-0.5123	0.0978	0.1347	1.5853	1.6397
2,5-NO_2	-0.1826	-0.7762	-0.1661	-0.1292	1.3214	1.3757
Naphthoquinones						
H	-0.1277	0.7182	1.3283	1.3652	2.8158	2.8702
2-NH_2	-0.1251	0.7882	1.3983	1.4352	2.8858	2.9401
2-OH	-0.1336	0.5558	1.1659	1.2028	2.6534	2.7078
2-CH_3	-0.1255	0.7784	1.3885	1.4254	2.8760	2.9303
2-CN	-0.1703	-0.4413	0.1688	0.2057	1.6563	1.7106
2-NO_2	-0.1606	-0.1788	0.4314	0.4682	1.9188	1.9732
5-NH_2	-0.1302	0.6502	1.2604	1.2972	2.7478	2.8022
5-OH	-0.1282	0.7033	1.3134	1.3503	2.8009	2.8553
5-CH_3	-0.1268	0.7426	1.3527	1.3896	2.8402	2.8946
5-CN	-0.1361	0.4896	1.0998	1.1366	2.5872	2.6416
5-NO_2	-0.1633	-0.2499	0.3602	0.3971	1.8476	1.9020
6-NH_2	-0.1242	0.8119	1.4220	1.4589	2.9095	2.9638
6-OH	-0.1291	0.6787	1.2888	1.3257	2.7763	2.8306
6-CH_3	-0.1274	0.7262	1.3363	1.3732	2.8237	2.8781
6-CN	-0.1376	0.4479	1.0580	1.0949	2.5455	2.5998
6-NO_2	-0.1493	0.1308	0.7409	0.7778	2.2283	2.2827
2,5,7-NH_2	-0.1052	1.3286	1.9387	1.9756	3.4262	3.4805
2,5,7-OH	-0.1191	0.9509	1.5610	1.5979	3.0485	3.1028
2,5,7-CH_3	-0.1171	1.0053	1.6154	1.6523	3.1029	3.1573
2,5,7-CN	-0.1588	-0.1285	0.4816	0.5185	1.9690	2.0234
2,5,7-NO_2	-0.1619	-0.2136	0.3965	0.4334	1.8839	1.9383
2,5,8-NH_2	-0.1001	1.4681	2.0782	2.1151	3.5657	3.6201
2,5,8-OH	-0.1153	1.0545	1.6647	1.7015	3.1521	3.2065
2,5,8-CH_3	-0.1156	1.0468	1.6569	1.6938	3.1444	3.1987
2,5,8-CN	-0.1572	-0.0858	0.5243	0.5612	2.0117	2.0661
2,5,8-NO_2	-0.1589	-0.1308	0.4793	0.5162	1.9668	2.0212
2,6,8-NH_2	-0.0975	1.5401	2.1502	2.1871	3.6376	3.6920
2,6,8-OH	-0.1153	1.0537	1.6638	1.7007	3.1513	3.2056
2,6,8-CH_3	-0.1170	1.0083	1.6185	1.6553	3.1059	3.1603
2,6,8-CN	-0.1581	-0.1096	0.5005	0.5374	1.9879	2.0423
2,6,8-NO_2	-0.1615	-0.2023	0.4078	0.4447	1.8952	1.9496
Anthraquinones						
H	-0.1183	0.9739	1.5840	1.6209	3.0714	3.1258
1-NH_2	-0.1214	0.8893	1.4994	1.5363	2.9869	3.0413
1-OH	-0.1192	0.9479	1.5581	1.5949	3.0455	3.0999
1-CH_3	-0.1565	-0.0666	0.5435	0.5804	2.0310	2.0853
1-CN	-0.1299	0.6583	1.2684	1.3053	2.7559	2.8102
1-NO_2	-0.1539	0.0045	0.6146	0.6515	2.1021	2.1564
2-NH_2	-0.1144	1.0785	1.6886	1.7255	3.1760	3.2304
2-OH	-0.1173	0.9995	1.6096	1.6465	3.0971	3.1514
2-CH_3	-0.1293	0.6747	1.2848	1.3217	2.7723	2.8267
2-CN	-0.1419	0.3311	0.9412	0.9781	2.4287	2.4831
2-NO_2	-0.1193	0.9461	1.5562	1.5931	3.0437	3.0980
1,3,5,7-NH_2	-0.0910	1.7150	2.3251	2.3620	3.8126	3.8670
1,3,5,7-OH	-0.1013	1.4370	2.0471	2.0840	3.5345	3.5889
1,3,5,7-CH_3	-0.1069	1.2840	1.8941	1.9310	3.3816	3.4359
1,3,5,7-CN	-0.1487	0.1453	0.7554	0.7923	2.2429	2.2973
1,3,5,7-NO_2	-0.1555	-0.0402	0.5699	0.6068	2.0574	2.1117

B.2.2 Second energy barrier

The following tables give the values of ΔE_2, which is the energy required to transfer an electron from one semiquinone radical (XH_2Q) to another to give a semiquinone singlet cation (XHQ^+) and a semiquinone singlet anion (XHQ^-).

Table B.13: ΔE_2 (eV) for coupled redox reactions involving oxidation of benzohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised BH_2Q	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	2,5-NH_2	2,5-OH	2,5-CH_3	2,5-CN	2,5-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.2121	0.2062	0.2209	0.2257	0.2435	0.2487	0.1875	0.2144	0.2200	0.2576	0.2653
Benzoquinones												
H	-0.1411	1.9296	1.7717	2.1709	2.3017	2.7863	2.9273	1.2614	1.9923	2.1466	3.1704	3.3795
2-NH_2	-0.2974	-2.3212	-2.4791	-2.0798	-1.9491	-1.4645	-1.3235	-2.9894	-2.2585	-2.1042	-1.0804	-0.8713
2-OH	-0.1391	1.9851	1.8272	2.2264	2.3571	2.8418	2.9828	1.3168	2.0478	2.2021	3.2259	3.4350
2-CH_3	-0.2825	-1.9157	-2.0736	-1.6744	-1.5437	-1.0590	-0.9180	-2.5840	-1.8530	-1.6987	-0.6749	-0.4658
2-CN	-0.2497	-1.0256	-1.1835	-0.7843	-0.6536	-0.1689	-0.0280	-1.6939	-0.9630	-0.8086	0.2152	0.4243
2-NO_2	-0.2431	-0.8443	-1.0022	-0.6030	-0.4723	0.0124	0.1533	-1.5126	-0.7817	-0.6273	0.3965	0.6056
2,5-NH_2	-0.3234	-3.0291	-3.1870	-2.7878	-2.6571	-2.1724	-2.0314	-3.6973	-2.9664	-2.8121	-1.7883	-1.5792
2,5-OH	-0.2936	-2.2187	-2.3766	-1.9774	-1.8467	-1.3620	-1.2210	-2.8870	-2.1560	-2.0017	-0.9779	-0.7688
2,5-CH_3	-0.2873	-2.0476	-2.2055	-1.8063	-1.6756	-1.1909	-1.0499	-2.7159	-1.9849	-1.8306	-0.8068	-0.5977
2,5-CN	-0.2286	-0.4495	-0.6074	-0.2082	-0.0775	0.4071	0.5481	-1.1178	-0.3869	-0.2326	0.7912	1.0003
2,5-NO_2	-0.2203	-0.2249	-0.3828	0.0164	0.1471	0.6318	0.7727	-0.8932	-0.1622	-0.0079	1.0159	1.2250
Naphthoquinones												
H	-0.1307	2.2149	2.0570	2.4562	2.5869	3.0715	3.2125	1.5466	2.2775	2.4318	3.4556	3.6647
2-NH_2	-0.1288	2.2649	2.1070	2.5062	2.6370	3.1216	3.2626	1.5967	2.3276	2.4819	3.5057	3.7148
2-OH	-0.1379	2.0182	1.8603	2.2595	2.3902	2.8749	3.0158	1.3499	2.0809	2.2352	3.2590	3.4681
2-CH_3	-0.1404	1.9506	1.7927	2.1919	2.3227	2.8073	2.9483	1.2824	2.0133	2.1676	3.1914	3.4005
2-CN	-0.1601	1.4147	1.2568	1.6560	1.7867	2.2714	2.4124	0.7464	1.4774	1.6317	2.6555	2.8646
2-NO_2	-0.1843	0.7562	0.5983	0.9975	1.1282	1.6129	1.7538	0.0879	0.8188	0.9732	1.9970	2.2060
5-NH_2	-0.1421	1.9038	1.7459	2.1451	2.2758	2.7604	2.9014	1.2355	1.9664	2.1207	3.1445	3.3536
5-OH	-0.1437	1.8593	1.7014	2.1006	2.2313	2.7160	2.8569	1.1910	1.9219	2.0763	3.1001	3.3091
5-CH_3	-0.1403	1.9521	1.7942	2.1934	2.3241	2.8087	2.9497	1.2838	2.0147	2.1690	3.1928	3.4019
5-CN	-0.1514	1.6507	1.4928	1.8920	2.0227	2.5074	2.6483	0.9824	1.7134	1.8677	2.8915	3.1006
5-NO_2	-0.1778	0.9315	0.7736	1.1728	1.3035	1.7882	1.9292	0.2632	0.9942	1.1485	2.1723	2.3814
6-NH_2	-0.1353	2.0888	1.9309	2.3301	2.4608	2.9454	3.0864	1.4205	2.1514	2.3057	3.3295	3.5386
6-OH	-0.1453	1.8159	1.6580	2.0572	2.1879	2.6726	2.8136	1.1476	1.8786	2.0329	3.0567	3.2658
6-CH_3	-0.1414	1.9225	1.7646	2.1638	2.2945	2.7792	2.9202	1.2542	1.9852	2.1395	3.1633	3.3724
6-CN	-0.1544	1.5678	1.4099	1.8091	1.9398	2.4245	2.5655	0.8995	1.6305	1.7848	2.8086	3.0177
6-NO_2	-0.1615	1.3746	1.2167	1.6159	1.7466	2.2313	2.3722	0.7063	1.4372	1.5916	2.6154	2.8244
2,5,7-NH_2	-0.0970	3.1301	2.9722	3.3714	3.5021	3.9868	4.1277	2.4618	3.1927	3.3471	4.3709	4.5800
2,5,7-OH	-0.1125	2.7089	2.5510	2.9502	3.0809	3.5656	3.7065	2.0406	2.7715	2.9259	3.9497	4.1588
2,5,7-CH_3	-0.1193	2.5231	2.3652	2.7644	2.8951	3.3798	3.5208	1.8548	2.5858	2.7401	3.7639	3.9730
2,5,7-CN	-0.1653	1.2726	1.1147	1.5139	1.6446	2.1292	2.2702	0.6043	1.3352	1.4895	2.5133	2.7224
2,5,7-NO_2	-0.1721	1.0864	0.9285	1.3277	1.4584	1.9431	2.0840	0.4181	1.1490	1.3034	2.3272	2.5363
2,5,8-NH_2	-0.0958	3.1625	3.0046	3.4038	3.5345	4.0192	4.1601	2.4942	3.2251	3.3795	4.4033	4.6123
2,5,8-OH	-0.1104	2.7670	2.6091	3.0083	3.1390	3.6237	3.7647	2.0988	2.8297	2.9840	4.0078	4.2169
2,5,8-CH_3	-0.1183	2.5499	2.3920	2.7912	2.9219	3.4066	3.5475	1.8816	2.6125	2.7669	3.7907	3.9997
2,5,8-CN	-0.1624	1.3519	1.1940	1.5932	1.7239	2.2086	2.3496	0.6836	1.4146	1.5689	2.5927	2.8018
2,5,8-NO_2	-0.1675	1.2128	1.0549	1.4541	1.5849	2.0695	2.2105	0.5446	1.2755	1.4298	2.4536	2.6627
2,6,8-NH_2	-0.0969	3.1344	2.9765	3.3757	3.5064	3.9910	4.1320	2.4661	3.1970	3.3513	4.3751	4.5842
2,6,8-OH	-0.1109	2.7520	2.5941	2.9933	3.1240	3.6087	3.7497	2.0837	2.8147	2.9690	3.9928	4.2019
2,6,8-CH_3	-0.1188	2.5377	2.3798	2.7791	2.9098	3.3944	3.5354	1.8695	2.6004	2.7547	3.7785	3.9876
2,6,8-CN	-0.1622	1.3577	1.1998	1.5990	1.7297	2.2144	2.3554	0.6894	1.4204	1.5747	2.5985	2.8076
2,6,8-NO_2	-0.1676	1.2085	1.0506	1.4498	1.5805	2.0652	2.2062	0.5403	1.2712	1.4255	2.4493	2.6584
Anthraquinones												
H	-0.1320	2.1777	2.0198	2.4190	2.5498	3.0344	3.1754	1.5095	2.2404	2.3947	3.4185	3.6276
1-NH_2	-0.1410	1.9326	1.7747	2.1739	2.3046	2.7893	2.9303	1.2643	1.9953	2.1496	3.1734	3.3825
1-OH	-0.1432	1.8743	1.7164	2.1156	2.2463	2.7310	2.8720	1.2060	1.9370	2.0913	3.1151	3.3242
1-CH_3	-0.1403	1.9537	1.7958	2.1950	2.3257	2.8103	2.9513	1.2854	2.0163	2.1706	3.1944	3.4035
1-CN	-0.1484	1.7334	1.5755	1.9747	2.1054	2.5901	2.7310	1.0651	1.7961	1.9504	2.9742	3.1833
1-NO_2	-0.1755	0.9940	0.8361	1.2353	1.3660	1.8507	1.9917	0.3257	1.0567	1.2110	2.2348	2.4439
2-NH_2	-0.1372	2.0372	1.8793	2.2785	2.4092	2.8939	3.0349	1.3689	2.0999	2.2542	3.2780	3.4871
2-OH	-0.1426	1.8886	1.7307	2.1299	2.2606	2.7453	2.8862	1.2203	1.9512	2.1056	3.1294	3.3385
2-CH_3	-0.1398	1.9657	1.8078	2.2070	2.3377	2.8224	2.9634	1.2974	2.0284	2.1827	3.2065	3.4156
2-CN	-0.1489	1.7186	1.5607	1.9599	2.0906	2.5753	2.7163	1.0503	1.7813	1.9356	2.9594	3.1685
2-NO_2	-0.1589	1.4474	1.2896	1.6888	1.8195	2.3041	2.4451	0.7792	1.5101	1.6644	2.6882	2.8973
1,3,5,7-NH_2	-0.0969	3.1345	2.9766	3.3758	3.5065	3.9912	4.1322	2.4662	3.1972	3.3515	4.3753	4.5844
1,3,5,7-OH	-0.1083	2.8235	2.6656	3.0648	3.1955	3.6801	3.8211	2.1552	2.8861	3.0404	4.0642	4.2733
1,3,5,7-CH_3	-0.1133	2.6883	2.5304	2.9297	3.0604	3.5450	3.6860	2.0201	2.7510	2.9053	3.9291	4.1382
1,3,5,7-CN	-0.1555	1.5398	1.3819	1.7811	1.9118	2.3965	2.5374	0.8715	1.6024	1.7568	2.7806	2.9897
1,3,5,7-NO_2	-0.1626	1.3446	1.1867	1.5860	1.7167	2.2013	2.3423	0.6764	1.4073	1.5616	2.5854	2.7945

Table B.14: ΔE_2 (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	5-NH_2	5-OH	5-CH_3	5-CN	5-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.2040	0.1610	0.1780	0.1833	0.2049	0.2009	0.1747	0.1813	0.1860	0.1998	0.1752
Benzoquinones												
H	-0.1411	1.7096	0.5413	1.0023	1.1466	1.7347	1.6255	0.9134	1.0921	1.2197	1.5950	0.9270
2-NH_2	-0.2974	-2.5412	-3.7095	-3.2484	-3.1042	-2.5161	-2.6253	-3.3374	-3.1587	-3.0311	-2.6558	-3.3237
2-OH	-0.1391	1.7650	0.5968	1.0578	1.2021	1.7901	1.6809	0.9688	1.1476	1.2751	1.6505	0.9825
2-CH_3	-0.2825	-2.1357	-3.3040	-2.8430	-2.6987	-2.1106	-2.2199	-2.9320	-2.7532	-2.6256	-2.2503	-2.9183
2-CN	-0.2497	-1.2457	-2.4140	-1.9529	-1.8086	-1.2206	-1.3298	-2.0419	-1.8631	-1.7356	-1.3602	-2.0282
2-NO_2	-0.2431	-1.0644	-2.2327	-1.7716	-1.6273	-1.0393	-1.1485	-1.8606	-1.6818	-1.5543	-1.1789	-1.8469
2,5-NH_2	-0.3234	-3.2491	-4.4174	-3.9564	-3.8121	-3.2240	-3.3332	-4.0454	-3.8666	-3.7390	-3.3637	-4.0317
2,5-OH	-0.2936	-2.4388	-3.6070	-3.1460	-3.0017	-2.4137	-2.5229	-3.2350	-3.0562	-2.9287	-2.5533	-3.2213
2,5-CH_3	-0.2873	-2.2677	-3.4359	-2.9749	-2.8306	-2.2426	-2.3518	-3.0639	-2.8851	-2.7576	-2.3822	-3.0502
2,5-CN	-0.2286	-0.6696	-1.8379	-1.3768	-1.2325	-0.6445	-0.7537	-1.4658	-1.2870	-1.1595	-0.7842	-1.4521
2,5-NO_2	-0.2203	-0.4450	-1.6133	-1.1522	-1.0079	-0.4199	-0.5291	-1.2412	-1.0624	-0.9349	-0.5595	-1.2275
Naphthoquinones												
H	-0.1307	1.9948	0.8265	1.2876	1.4319	2.0199	1.9107	1.1986	1.3774	1.5049	1.8802	1.2123
2-NH_2	-0.1288	2.0449	0.8766	1.3376	1.4819	2.0700	1.9608	1.2486	1.4274	1.5550	1.9303	1.2623
2-OH	-0.1379	1.7981	0.6298	1.0909	1.2352	1.8232	1.7140	1.0019	1.1807	1.3082	1.6836	1.0156
2-CH_3	-0.1404	1.7306	0.5623	1.0233	1.1676	1.7557	1.6465	0.9344	1.1131	1.2407	1.6160	0.9480
2-CN	-0.1601	1.1946	0.0264	0.4874	0.6317	1.2197	1.1105	0.3984	0.5772	0.7047	1.0801	0.4121
2-NO_2	-0.1843	0.5361	-0.6322	-0.1711	-0.0268	0.5612	0.4520	-0.2601	-0.0813	0.0462	0.4216	-0.2464
5-NH_2	-0.1421	1.6837	0.5154	0.9765	1.1208	1.7088	1.5996	0.8875	1.0663	1.1938	1.5691	0.9012
5-OH	-0.1437	1.6392	0.4709	0.9320	1.0763	1.6643	1.5551	0.8430	1.0218	1.1493	1.5246	0.8567
5-CH_3	-0.1403	1.7320	0.5637	1.0248	1.1691	1.7571	1.6479	0.9358	1.1146	1.2421	1.6174	0.9495
5-CN	-0.1514	1.4306	0.2623	0.7234	0.8677	1.4557	1.3465	0.6344	0.8132	0.9407	1.3161	0.6481
5-NO_2	-0.1778	0.7114	-0.4569	0.0042	0.1485	0.7365	0.6273	-0.0848	0.0940	0.2215	0.5969	-0.0711
6-NH_2	-0.1353	1.8687	0.7004	1.1615	1.3058	1.8938	1.7846	1.0725	1.2513	1.3788	1.7541	1.0862
6-OH	-0.1453	1.5959	0.4276	0.8886	1.0329	1.6210	1.5117	0.7996	0.9784	1.1059	1.4813	0.8133
6-CH_3	-0.1414	1.7024	0.5342	0.9952	1.1395	1.7275	1.6183	0.9062	1.0850	1.2125	1.5879	0.9199
6-CN	-0.1544	1.3478	0.1795	0.6405	0.7848	1.3728	1.2636	0.5515	0.7303	0.8578	1.2332	0.5652
6-NO_2	-0.1615	1.1545	-0.0138	0.4473	0.5916	1.1796	1.0704	0.3583	0.5371	0.6646	1.0399	0.3720
2,5,7-NH_2	-0.0970	2.9100	1.7417	2.2028	2.3471	2.9351	2.8259	2.1138	2.2926	2.4201	2.7955	2.1275
2,5,7-OH	-0.1125	2.4888	1.3205	1.7816	1.9259	2.5139	2.4047	1.6926	1.8714	1.9989	2.3743	1.7063
2,5,7-CH_3	-0.1193	2.3030	1.1348	1.5958	1.7401	2.3281	2.2189	1.5068	1.6856	1.8131	2.1885	1.5205
2,5,7-CN	-0.1653	1.0525	-0.1158	0.3453	0.4896	1.0776	0.9684	0.2563	0.4351	0.5626	0.9379	0.2700
2,5,7-NO_2	-0.1721	0.8663	-0.3020	0.1591	0.3034	0.8914	0.7822	0.0701	0.2489	0.3764	0.7518	0.0838
2,5,8-NH_2	-0.0958	2.9424	1.7741	2.2352	2.3795	2.9675	2.8583	2.1462	2.3250	2.4525	2.8279	2.1599
2,5,8-OH	-0.1104	2.5470	1.3787	1.8397	1.9840	2.5721	2.4628	1.7507	1.9295	2.0571	2.4324	1.7644
2,5,8-CH_3	-0.1183	2.3298	1.1615	1.6226	1.7669	2.3549	2.2457	1.5336	1.7124	1.8399	2.2152	1.5473
2,5,8-CN	-0.1624	1.1319	-0.0364	0.4246	0.5689	1.1570	1.0477	0.3356	0.5144	0.6419	1.0173	0.3493
2,5,8-NO_2	-0.1675	0.9928	-0.1755	0.2855	0.4298	1.0179	0.9087	0.1966	0.3753	0.5029	0.8782	0.2102
2,6,8-NH_2	-0.0969	2.9143	1.7460	2.2071	2.3514	2.9394	2.8302	2.1181	2.2969	2.4244	2.7997	2.1318
2,6,8-OH	-0.1109	2.5319	1.3637	1.8247	1.9690	2.5570	2.4478	1.7357	1.9145	2.0420	2.4174	1.7494
2,6,8-CH_3	-0.1188	2.3177	1.1494	1.6105	1.7547	2.3428	2.2336	1.5215	1.7002	1.8278	2.2031	1.5352
2,6,8-CN	-0.1622	1.1377	-0.0306	0.4304	0.5747	1.1628	1.0535	0.3414	0.5202	0.6478	1.0231	0.3551
2,6,8-NO_2	-0.1676	0.9885	-0.1798	0.2812	0.4255	1.0136	0.9044	0.1922	0.3710	0.4986	0.8739	0.2059
Anthraquinones												
H	-0.1320	1.9577	0.7894	1.2504	1.3947	1.9828	1.8736	1.1615	1.3402	1.4678	1.8431	1.1751
1-NH_2	-0.1410	1.7126	0.5443	1.0053	1.1496	1.7377	1.6284	0.9163	1.0951	1.2226	1.5980	0.9300
1-OH	-0.1432	1.6542	0.4860	0.9470	1.0913	1.6793	1.5701	0.8580	1.0368	1.1643	1.5397	0.8717
1-CH_3	-0.1403	1.7336	0.5653	1.0264	1.1707	1.7587	1.6495	0.9374	1.1162	1.2437	1.6190	0.9511
1-CN	-0.1484	1.5133	0.3450	0.8061	0.9504	1.5384	1.4292	0.7171	0.8959	1.0234	1.3988	0.7308
1-NO_2	-0.1755	0.7739	-0.3943	0.0667	0.2110	0.7990	0.6898	-0.0223	0.1565	0.2840	0.6594	-0.0086
2-NH_2	-0.1372	1.8172	0.6489	1.1099	1.2542	1.8423	1.7330	1.0209	1.1997	1.3273	1.7026	1.0346
2-OH	-0.1426	1.6685	0.5002	0.9613	1.1056	1.6936	1.5844	0.8723	1.0511	1.1786	1.5540	0.8860
2-CH_3	-0.1398	1.7457	0.5774	1.0384	1.1827	1.7708	1.6615	0.9494	1.1282	1.2558	1.6311	0.9631
2-CN	-0.1489	1.4985	0.3302	0.7913	0.9356	1.5236	1.4144	0.7023	0.8811	1.0086	1.3840	0.7160
2-NO_2	-0.1589	1.2274	0.0591	0.5202	0.6645	1.2525	1.1433	0.4312	0.6099	0.7375	1.1128	0.4449
1,3,5,7-NH_2	-0.0969	2.9145	1.7462	2.2072	2.3515	2.9396	2.8303	2.1182	2.2970	2.4245	2.7999	2.1319
1,3,5,7-OH	-0.1083	2.6034	1.4351	1.8962	2.0405	2.6285	2.5193	1.8072	1.9860	2.1135	2.4888	1.8209
1,3,5,7-CH_3	-0.1133	2.4683	1.3000	1.7611	1.9053	2.4934	2.3842	1.6721	1.8508	1.9784	2.3537	1.6858
1,3,5,7-CN	-0.1555	1.3197	0.1514	0.6125	0.7568	1.3448	1.2356	0.5235	0.7023	0.8298	1.2052	0.5372
1,3,5,7-NO_2	-0.1626	1.1246	-0.0437	0.4174	0.5616	1.1497	1.0405	0.3284	0.5071	0.6347	1.0100	0.3421

Table B.15: ΔE_2 (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	6-NH_2	6-OH	6-CH_3	6-CN	6-NO_2	2,5,7-NH_2	2,5,7-OH	2,5,7-CH_3	2,5,7-CN	2,5,7-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.1725	0.1884	0.1870	0.2007	0.1947	0.1648	0.1891	0.1916	0.2409	0.2475
Benzoquinones											
H	-0.1411	0.8538	1.2861	1.2482	1.6215	1.4565	0.6427	1.3055	1.3724	2.7149	2.8951
2-NH_2	-0.2974	-3.3970	-2.9647	-3.0026	-2.6293	-2.7943	-3.6081	-2.9453	-2.8783	-1.5359	-1.3557
2-OH	-0.1391	0.9093	1.3416	1.3037	1.6769	1.5120	0.6982	1.3610	1.4279	2.7704	2.9506
2-CH_3	-0.2825	-2.9915	-2.5592	-2.5971	-2.2239	-2.3888	-3.2026	-2.5398	-2.4729	-1.1304	-0.9502
2-CN	-0.2497	-2.1015	-1.6691	-1.7070	-1.3338	-1.4987	-2.3125	-1.6497	-1.5828	-0.2403	-0.0602
2-NO_2	-0.2431	-1.9202	-1.4878	-1.5257	-1.1525	-1.3174	-2.1312	-1.4684	-1.4015	-0.0590	0.1211
2,5-NH_2	-0.3234	-4.1049	-3.6726	-3.7105	-3.3372	-3.5022	-4.3160	-3.6532	-3.5863	-2.2438	-2.0636
2,5-OH	-0.2936	-3.2945	-2.8622	-2.9001	-2.5269	-2.6918	-3.5056	-2.8428	-2.7759	-1.4334	-1.2532
2,5-CH_3	-0.2873	-3.1234	-2.6911	-2.7290	-2.3558	-2.5207	-3.3345	-2.6717	-2.6048	-1.2623	-1.0821
2,5-CN	-0.2286	-1.5254	-1.0931	-1.1310	-0.7577	-0.9227	-1.7365	-1.0737	-1.0067	0.3357	0.5159
2,5-NO_2	-0.2203	-1.3007	-0.8684	-0.9063	-0.5331	-0.6980	-1.5118	-0.8490	-0.7821	0.5604	0.7405
Naphthoquinones											
H	-0.1307	1.1390	1.5713	1.5334	1.9067	1.7417	0.9279	1.5907	1.6577	3.0001	3.1803
2-NH_2	-0.1288	1.1891	1.6214	1.5835	1.9568	1.7918	0.9780	1.6408	1.7077	3.0502	3.2304
2-OH	-0.1379	0.9424	1.3747	1.3368	1.7100	1.5451	0.7313	1.3941	1.4610	2.8035	2.9836
2-CH_3	-0.1404	0.8748	1.3071	1.2692	1.6425	1.4775	0.6637	1.3265	1.3934	2.7359	2.9161
2-CN	-0.1601	0.3389	0.7712	0.7333	1.1065	0.9416	0.1278	0.7906	0.8575	2.2000	2.3802
2-NO_2	-0.1843	-0.3197	0.1127	0.0747	0.4480	0.2831	-0.5307	0.1321	0.1990	1.5415	1.7216
5-NH_2	-0.1421	0.8279	1.2602	1.2223	1.5956	1.4306	0.6168	1.2796	1.3466	2.6890	2.8692
5-OH	-0.1437	0.7834	1.2158	1.1778	1.5511	1.3861	0.5724	1.2352	1.3021	2.6445	2.8247
5-CH_3	-0.1403	0.8762	1.3085	1.2706	1.6439	1.4789	0.6651	1.3279	1.3949	2.7373	2.9175
5-CN	-0.1514	0.5749	1.0072	0.9693	1.3425	1.1776	0.3638	1.0266	1.0935	2.4360	2.6161
5-NO_2	-0.1778	-0.1443	0.2880	0.2501	0.6233	0.4584	-0.3554	0.3074	0.3743	1.7168	1.8969
6-NH_2	-0.1353	1.0129	1.4452	1.4073	1.7806	1.6156	0.8018	1.4646	1.5316	2.8740	3.0542
6-OH	-0.1453	0.7401	1.1724	1.1345	1.5077	1.3428	0.5290	1.1918	1.2587	2.6012	2.7814
6-CH_3	-0.1414	0.8467	1.2790	1.2411	1.6143	1.4494	0.6356	1.2984	1.3653	2.7078	2.8880
6-CN	-0.1544	0.4920	0.9243	0.8864	1.2596	1.0947	0.2809	0.9437	1.0106	2.3531	2.5333
6-NO_2	-0.1615	0.2987	0.7311	0.6931	1.0664	0.9015	0.0877	0.7505	0.8174	2.1598	2.3400
2,5,7-NH_2	-0.0970	2.0543	2.4866	2.4487	2.8219	2.6570	1.8432	2.5060	2.5729	3.9154	4.0955
2,5,7-OH	-0.1125	1.6330	2.0654	2.0275	2.4007	2.2358	1.4220	2.0848	2.1517	3.4942	3.6743
2,5,7-CH_3	-0.1193	1.4473	1.8796	1.8417	2.2149	2.0500	1.2362	1.8990	1.9659	3.3084	3.4886
2,5,7-CN	-0.1653	0.1967	0.6290	0.5911	0.9644	0.7994	-0.0144	0.6485	0.7154	2.0578	2.2380
2,5,7-NO_2	-0.1721	0.0105	0.4429	0.4049	0.7782	0.6133	-0.2005	0.4623	0.5292	1.8717	2.0518
2,5,8-NH_2	-0.0958	2.0866	2.5190	2.4810	2.8543	2.6894	1.8756	2.5384	2.6053	3.9478	4.1279
2,5,8-OH	-0.1104	1.6912	2.1235	2.0856	2.4589	2.2939	1.4801	2.1429	2.2098	3.5523	3.7325
2,5,8-CH_3	-0.1183	1.4740	1.9064	1.8684	2.2417	2.0767	1.2630	1.9258	1.9927	3.3351	3.5153
2,5,8-CN	-0.1624	0.2761	0.7084	0.6705	1.0437	0.8788	0.0650	0.7278	0.7947	2.1372	2.3174
2,5,8-NO_2	-0.1675	0.1370	0.5693	0.5314	0.9047	0.7397	-0.0741	0.5887	0.6556	1.9981	2.1783
2,6,8-NH_2	-0.0969	2.0585	2.4908	2.4529	2.8262	2.6612	1.8474	2.5102	2.5772	3.9196	4.0998
2,6,8-OH	-0.1109	1.6762	2.1085	2.0706	2.4438	2.2789	1.4651	2.1279	2.1948	3.5373	3.7175
2,6,8-CH_3	-0.1188	1.4619	1.8942	1.8563	2.2296	2.0646	1.2508	1.9136	1.9806	3.3230	3.5032
2,6,8-CN	-0.1622	0.2819	0.7142	0.6763	1.0495	0.8846	0.0708	0.7336	0.8005	2.1430	2.3232
2,6,8-NO_2	-0.1676	0.1327	0.5650	0.5271	0.9004	0.7354	-0.0784	0.5844	0.6513	1.9938	2.1740
Anthraquinones											
H	-0.1320	1.1019	1.5342	1.4963	1.8696	1.7046	0.8908	1.5536	1.6205	2.9630	3.1432
1-NH_2	-0.1410	0.8568	1.2891	1.2512	1.6244	1.4595	0.6457	1.3085	1.3754	2.7179	2.8981
1-OH	-0.1432	0.7985	1.2308	1.1929	1.5661	1.4012	0.5874	1.2502	1.3171	2.6596	2.8398
1-CH_3	-0.1403	0.8778	1.3101	1.2722	1.6455	1.4805	0.6667	1.3295	1.3965	2.7389	2.9191
1-CN	-0.1484	0.6576	1.0899	1.0520	1.4252	1.2603	0.4465	1.1093	1.1762	2.5187	2.6988
1-NO_2	-0.1755	-0.0818	0.3505	0.3126	0.6858	0.5209	-0.2929	0.3699	0.4368	1.7793	1.9595
2-NH_2	-0.1372	0.9614	1.3937	1.3558	1.7290	1.5641	0.7503	1.4131	1.4800	2.8225	3.0027
2-OH	-0.1426	0.8127	1.2451	1.2072	1.5804	1.4155	0.6017	1.2645	1.3314	2.6739	2.8540
2-CH_3	-0.1398	0.8899	1.3222	1.2843	1.6575	1.4926	0.6788	1.3416	1.4085	2.7510	2.9312
2-CN	-0.1489	0.6428	1.0751	1.0372	1.4104	1.2455	0.4317	1.0945	1.1614	2.5039	2.6840
2-NO_2	-0.1589	0.3716	0.8039	0.7660	1.1393	0.9743	0.1605	0.8233	0.8903	2.2327	2.4129
1,3,5,7-NH_2	-0.0969	2.0587	2.4910	2.4531	2.8263	2.6614	1.8476	2.5104	2.5773	3.9198	4.1000
1,3,5,7-OH	-0.1083	1.7476	2.1799	2.1420	2.5153	2.3503	1.5365	2.1993	2.2663	3.6087	3.7889
1,3,5,7-CH_3	-0.1133	1.6125	2.0448	2.0069	2.3802	2.2152	1.4014	2.0642	2.1312	3.4736	3.6538
1,3,5,7-CN	-0.1555	0.4639	0.8963	0.8584	1.2316	1.0667	0.2529	0.9157	0.9826	2.3251	2.5052
1,3,5,7-NO_2	-0.1626	0.2688	0.7011	0.6632	1.0365	0.8715	0.0577	0.7205	0.7875	2.1299	2.3101

Table B.16: ΔE_2 (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised NH_2Q	2,5,8-NH_2	2,5,8-OH	2,5,8-CH_3	2,5,8-CN	2,5,8-NO_2	2,6,8-NH_2	2,6,8-OH	2,6,8-CH_3	2,6,8-CN	2,6,8-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.1542	0.1844	0.1897	0.2403	0.2457	0.1626	0.1901	0.1927	0.2407	0.2456
Benzoquinones											
H	-0.1411	0.3558	1.1767	1.3212	2.6981	2.8453	0.5831	1.3328	1.4031	2.7083	2.8431
2-NH_2	-0.2974	-3.8950	-3.0741	-2.9296	-1.5527	-1.4055	-3.6677	-2.9180	-2.8477	-1.5425	-1.4077
2-OH	-0.1391	0.4113	1.2321	1.3767	2.7536	2.9007	0.6386	1.3882	1.4586	2.7637	2.8986
2-CH_3	-0.2825	-3.4895	-2.6686	-2.5241	-1.1472	-1.0001	-3.2622	-2.5126	-2.4422	-1.1371	-1.0022
2-CN	-0.2497	-2.5994	-1.7786	-1.6341	-0.2571	-0.1100	-2.3722	-1.6225	-1.5521	-0.2470	-0.1122
2-NO_2	-0.2431	-2.4181	-1.5973	-1.4528	-0.0758	0.0713	-2.1909	-1.4412	-1.3708	-0.0657	0.0691
2,5-NH_2	-0.3234	-4.6029	-3.7820	-3.6375	-2.2606	-2.1135	-4.3756	-3.6259	-3.5556	-2.2504	-2.1156
2,5-OH	-0.2936	-3.7925	-2.9716	-2.8271	-1.4502	-1.3031	-3.5652	-2.8156	-2.7452	-1.4401	-1.3052
2,5-CH_3	-0.2873	-3.6214	-2.8006	-2.6560	-1.2791	-1.1320	-3.3941	-2.6445	-2.5741	-1.2690	-1.1341
2,5-CN	-0.2286	-2.0234	-1.2025	-1.0580	0.3190	0.4661	-1.7961	-1.0464	-0.9760	0.3291	0.4639
2,5-NO_2	-0.2203	-1.7987	-0.9779	-0.8333	0.5436	0.6907	-1.5714	-0.8218	-0.7514	0.5537	0.6885
Naphthoquinones											
H	-0.1307	0.6411	1.4619	1.6064	2.9834	3.1305	0.8683	1.6180	1.6884	2.9935	3.1283
2-NH_2	-0.1288	0.6911	1.5120	1.6565	3.0334	3.1806	0.9184	1.6681	1.7384	3.0436	3.1784
2-OH	-0.1379	0.4444	1.2652	1.4098	2.7867	2.9338	0.6717	1.4213	1.4917	2.7968	2.9316
2-CH_3	-0.1404	0.3768	1.1977	1.3422	2.7191	2.8663	0.6041	1.3538	1.4241	2.7293	2.8641
2-CN	-0.1601	-0.1591	0.6617	0.8063	2.1832	2.3303	0.0682	0.8178	0.8882	2.1933	2.3282
2-NO_2	-0.1843	-0.8176	0.0032	0.1477	1.5247	1.6718	-0.5904	0.1593	0.2297	1.5348	1.6696
5-NH_2	-0.1421	0.3300	1.1508	1.2953	2.6723	2.8194	0.5572	1.3069	1.3773	2.6824	2.8172
5-OH	-0.1437	0.2855	1.1063	1.2508	2.6278	2.7749	0.5127	1.2624	1.3328	2.6379	2.7727
5-CH_3	-0.1403	0.3783	1.1991	1.3436	2.7206	2.8677	0.6055	1.3552	1.4256	2.7307	2.8655
5-CN	-0.1514	0.0769	0.8977	1.0423	2.4192	2.5663	0.3042	1.0538	1.1242	2.4293	2.5641
5-NO_2	-0.1778	-0.6423	0.1785	0.3231	1.7000	1.8471	-0.4150	0.3346	0.4050	1.7101	1.8450
6-NH_2	-0.1353	0.5150	1.3358	1.4803	2.8573	3.0044	0.7422	1.4919	1.5623	2.8674	3.0022
6-OH	-0.1453	0.2421	1.0630	1.2075	2.5844	2.7315	0.4694	1.2190	1.2894	2.5945	2.7294
6-CH_3	-0.1414	0.3487	1.1695	1.3141	2.6910	2.8381	0.5760	1.3256	1.3960	2.7011	2.8360
6-CN	-0.1544	-0.0060	0.8149	0.9594	2.3363	2.4834	0.2213	0.9709	1.0413	2.3464	2.4813
6-NO_2	-0.1615	-0.1992	0.6216	0.7661	2.1431	2.2902	0.0280	0.7777	0.8481	2.1532	2.2880
2,5,7-NH_2	-0.0970	1.5563	2.3771	2.5217	3.8986	4.0457	1.7836	2.5332	2.6036	3.9087	4.0435
2,5,7-OH	-0.1125	1.1351	1.9559	2.1004	3.4774	3.6245	1.3623	2.1120	2.1824	3.4875	3.6223
2,5,7-CH_3	-0.1193	0.9493	1.7702	1.9147	3.2916	3.4387	1.1766	1.9262	1.9966	3.3017	3.4366
2,5,7-CN	-0.1653	-0.3012	0.5196	0.6641	2.0411	2.1882	-0.0740	0.6757	0.7461	2.0512	2.1860
2,5,7-NO_2	-0.1721	-0.4874	0.3334	0.4779	1.8549	2.0020	-0.2602	0.4895	0.5599	1.8650	1.9998
2,5,8-NH_2	-0.0958	1.5887	2.4095	2.5540	3.9310	4.0781	1.8159	2.5656	2.6360	3.9411	4.0759
2,5,8-OH	-0.1104	1.1932	2.0141	2.1586	3.5355	3.6826	1.4205	2.1702	2.2405	3.5457	3.6805
2,5,8-CH_3	-0.1183	0.9761	1.7969	1.9414	3.3184	3.4655	1.2033	1.9530	2.0234	3.3285	3.4633
2,5,8-CN	-0.1624	-0.2219	0.5990	0.7435	2.1204	2.2675	0.0054	0.7550	0.8254	2.1305	2.2654
2,5,8-NO_2	-0.1675	-0.3610	0.4599	0.6044	1.9813	2.1285	-0.1337	0.6160	0.6863	1.9915	2.1263
2,6,8-NH_2	-0.0969	1.5606	2.3814	2.5259	3.9029	4.0500	1.7878	2.5375	2.6079	3.9130	4.0478
2,6,8-OH	-0.1109	1.1782	1.9991	2.1436	3.5205	3.6676	1.4055	2.1551	2.2255	3.5306	3.6655
2,6,8-CH_3	-0.1188	0.9639	1.7848	1.9293	3.3062	3.4534	1.1912	1.9409	2.0112	3.3164	3.4512
2,6,8-CN	-0.1622	-0.2161	0.6048	0.7493	2.1262	2.2733	0.0112	0.7608	0.8312	2.1363	2.2712
2,6,8-NO_2	-0.1676	-0.3653	0.4556	0.6001	1.9770	2.1241	-0.1380	0.6117	0.6820	1.9872	2.1220
Anthraquinones											
H	-0.1320	0.6039	1.4248	1.5693	2.9462	3.0934	0.8312	1.5809	1.6512	2.9564	3.0912
1-NH_2	-0.1410	0.3588	1.1797	1.3242	2.7011	2.8482	0.5861	1.3357	1.4061	2.7112	2.8461
1-OH	-0.1432	0.3005	1.1214	1.2659	2.6428	2.7899	0.5278	1.2774	1.3478	2.6529	2.7878
1-CH_3	-0.1403	0.3798	1.2007	1.3452	2.7222	2.8693	0.6071	1.3568	1.4272	2.7323	2.8671
1-CN	-0.1484	0.1596	0.9804	1.1250	2.5019	2.6490	0.3869	1.1365	1.2069	2.5120	2.6468
1-NO_2	-0.1755	-0.5798	0.2411	0.3856	1.7625	1.9096	-0.3525	0.3971	0.4675	1.7726	1.9075
2-NH_2	-0.1372	0.4634	1.2843	1.4288	2.8057	2.9528	0.6907	1.4403	1.5107	2.8158	2.9507
2-OH	-0.1426	0.3148	1.1356	1.2801	2.6571	2.8042	0.5420	1.2917	1.3621	2.6672	2.8020
2-CH_3	-0.1398	0.3919	1.2128	1.3573	2.7342	2.8813	0.6192	1.3688	1.4392	2.7443	2.8792
2-CN	-0.1489	0.1448	0.9656	1.1102	2.4871	2.6342	0.3721	1.1217	1.1921	2.4972	2.6320
2-NO_2	-0.1589	-0.1264	0.6945	0.8390	2.2160	2.3631	0.1009	0.8506	0.9210	2.2261	2.3609
1,3,5,7-NH_2	-0.0969	1.5607	2.3816	2.5261	3.9030	4.0501	1.7880	2.5376	2.6080	3.9131	4.0480
1,3,5,7-OH	-0.1083	1.2497	2.0705	2.2150	3.5920	3.7391	1.4769	2.2266	2.2970	3.6021	3.7369
1,3,5,7-CH_3	-0.1133	1.1145	1.9354	2.0799	3.4568	3.6040	1.3418	2.0915	2.1618	3.4670	3.6018
1,3,5,7-CN	-0.1555	-0.0340	0.7868	0.9313	2.3083	2.4554	0.1932	0.9429	1.0133	2.3184	2.4532
1,3,5,7-NO_2	-0.1626	-0.2292	0.5917	0.7362	2.1131	2.2603	-0.0019	0.7478	0.8181	2.1233	2.2581

Table B.17: ΔE_2 (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised AH_2Q	H	1-NH_2	1-OH	1-CH_3	1-CN	1-NO_2	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.1949	0.1577	0.1610	0.1640	0.1776	0.1522	0.1627	0.1657	0.1654	0.1778	0.1719
Benzoquinones												
H	-0.1411	1.4620	0.4494	0.5402	0.6211	0.9913	0.3015	0.5877	0.6682	0.6603	0.9987	0.8368
2-NH_2	-0.2974	-2.7888	-3.8014	-3.7106	-3.6296	-3.2595	-3.9493	-3.6631	-3.5826	-3.5905	-3.2521	-3.4140
2-OH	-0.1391	1.5174	0.5049	0.5956	0.6766	1.0467	0.3569	0.6432	0.7236	0.7157	1.0541	0.8923
2-CH_3	-0.2825	-2.3834	-3.3959	-3.3051	-3.2242	-2.8540	-3.5439	-3.2576	-3.1771	-3.1850	-2.8466	-3.0085
2-CN	-0.2497	-1.4933	-2.5058	-2.4151	-2.3341	-1.9640	-2.6538	-2.3676	-2.2871	-2.2950	-1.9566	-2.1184
2-NO_2	-0.2431	-1.3120	-2.3245	-2.2338	-2.1528	-1.7827	-2.4725	-2.1863	-2.1058	-2.1137	-1.7753	-1.9371
2,5-NH_2	-0.3234	-3.4968	-4.5093	-4.4185	-4.3376	-3.9674	-4.6573	-4.3710	-4.2905	-4.2984	-3.9600	-4.1219
2,5-OH	-0.2936	-2.6864	-3.6989	-3.6082	-3.5272	-3.1570	-3.8469	-3.5606	-3.4802	-3.4881	-3.1497	-3.3115
2,5-CH_3	-0.2873	-2.5153	-3.5278	-3.4371	-3.3561	-2.9859	-3.6758	-3.3895	-3.3091	-3.3170	-2.9786	-3.1404
2,5-CN	-0.2286	-0.9172	-1.9298	-1.8390	-1.7580	-1.3879	-2.0777	-1.7915	-1.7110	-1.7189	-1.3805	-1.5424
2,5-NO_2	-0.2203	-0.6926	-1.7051	-1.6144	-1.5334	-1.1633	-1.8531	-1.5669	-1.4864	-1.4943	-1.1559	-1.3177
Naphthoquinones												
H	-0.1307	1.7472	0.7346	0.8254	0.9064	1.2765	0.5867	0.8729	0.9534	0.9455	1.2839	1.1220
2-NH_2	-0.1288	1.7972	0.7847	0.8755	0.9564	1.3266	0.6367	0.9230	1.0035	0.9956	1.3340	1.1721
2-OH	-0.1379	1.5505	0.5380	0.6287	0.7097	1.0798	0.3900	0.6762	0.7567	0.7488	1.0872	0.9254
2-CH_3	-0.1404	1.4830	0.4704	0.5612	0.6421	1.0123	0.3225	0.6087	0.6892	0.6813	1.0197	0.8578
2-CN	-0.1601	0.9470	-0.0655	0.0252	0.1062	0.4763	-0.2135	0.0728	0.1532	0.1453	0.4837	0.3219
2-NO_2	-0.1843	0.2885	-0.7240	-0.6333	-0.5523	-0.1822	-0.8720	-0.5858	-0.5053	-0.5132	-0.1748	-0.3366
5-NH_2	-0.1421	1.4361	0.4235	0.5143	0.5953	0.9654	0.2756	0.5618	0.6423	0.6344	0.9728	0.8109
5-OH	-0.1437	1.3916	0.3791	0.4698	0.5508	0.9209	0.2311	0.5173	0.5978	0.5899	0.9283	0.7665
5-CH_3	-0.1403	1.4844	0.4718	0.5626	0.6436	1.0137	0.3239	0.6101	0.6906	0.6827	1.0211	0.8592
5-CN	-0.1514	1.1830	0.1705	0.2612	0.3422	0.7123	0.0225	0.3087	0.3892	0.3813	0.7197	0.5579
5-NO_2	-0.1778	0.4638	-0.5487	-0.4580	-0.3770	-0.0069	-0.6967	-0.4104	-0.3300	-0.3379	0.0005	-0.1613
6-NH_2	-0.1353	1.6211	0.6085	0.6993	0.7803	1.1504	0.4606	0.7468	0.8273	0.8194	1.1578	0.9959
6-OH	-0.1453	1.3482	0.3357	0.4265	0.5074	0.8776	0.1877	0.4740	0.5544	0.5466	0.8849	0.7231
6-CH_3	-0.1414	1.4548	0.4423	0.5330	0.6140	0.9841	0.2943	0.5806	0.6610	0.6531	0.9915	0.8297
6-CN	-0.1544	1.1001	0.0876	0.1784	0.2593	0.6295	-0.0604	0.2259	0.3063	0.2984	0.6368	0.4750
6-NO_2	-0.1615	0.9069	-0.1056	-0.0149	0.0661	0.4362	-0.2536	0.0326	0.1131	0.1052	0.4436	0.2818
2,5,7-NH_2	-0.0970	2.6624	1.6499	1.7406	1.8216	2.1917	1.5019	1.7881	1.8686	1.8607	2.1991	2.0373
2,5,7-OH	-0.1125	2.2412	1.2287	1.3194	1.4004	1.7705	1.0807	1.3669	1.4474	1.4395	1.7779	1.6161
2,5,7-CH_3	-0.1193	2.0554	1.0429	1.1337	1.2146	1.5848	0.8949	1.1812	1.2616	1.2537	1.5921	1.4303
2,5,7-CN	-0.1653	0.8049	-0.2076	-0.1169	-0.0359	0.3342	-0.3556	-0.0694	0.0111	0.0032	0.3416	0.1797
2,5,7-NO_2	-0.1721	0.6187	-0.3938	-0.3031	-0.2221	0.1480	-0.5418	-0.2556	-0.1751	-0.1830	0.1554	-0.0064
2,5,8-NH_2	-0.0958	2.6948	1.6823	1.7730	1.8540	2.2241	1.5343	1.8205	1.9010	1.8931	2.2315	2.0697
2,5,8-OH	-0.1104	2.2993	1.2868	1.3776	1.4585	1.8287	1.1388	1.4251	1.5056	1.4977	1.8361	1.6742
2,5,8-CH_3	-0.1183	2.0822	1.0697	1.1604	1.2414	1.6115	0.9217	1.2079	1.2884	1.2805	1.6189	1.4571
2,5,8-CN	-0.1624	0.8842	-0.1283	-0.0375	0.0434	0.4136	-0.2763	0.0100	0.0904	0.0825	0.4209	0.2591
2,5,8-NO_2	-0.1675	0.7452	-0.2674	-0.1766	-0.0957	0.2745	-0.4154	-0.1291	-0.0486	-0.0565	0.2819	0.1200
2,6,8-NH_2	-0.0969	2.6667	1.6541	1.7449	1.8259	2.1960	1.5062	1.7924	1.8729	1.8650	2.2034	2.0415
2,6,8-OH	-0.1109	2.2843	1.2718	1.3625	1.4435	1.8137	1.1238	1.4101	1.4905	1.4826	1.8210	1.6592
2,6,8-CH_3	-0.1188	2.0701	1.0575	1.1483	1.2292	1.5994	0.9096	1.1958	1.2763	1.2684	1.6068	1.4449
2,6,8-CN	-0.1622	0.8900	-0.1225	-0.0317	0.0492	0.4194	-0.2705	0.0158	0.0963	0.0884	0.4268	0.2649
2,6,8-NO_2	-0.1676	0.7408	-0.2717	-0.1809	-0.1000	0.2702	-0.4197	-0.1334	-0.0529	-0.0608	0.2776	0.1157
Anthraquinones												
H	-0.1320	1.7101	0.6975	0.7883	0.8692	1.2394	0.5496	0.8358	0.9163	0.9084	1.2468	1.0849
1-NH_2	-0.1410	1.4649	0.4524	0.5432	0.6241	0.9943	0.3044	0.5907	0.6711	0.6633	1.0017	0.8398
1-OH	-0.1432	1.4066	0.3941	0.4849	0.5658	0.9360	0.2461	0.5324	0.6128	0.6049	0.9433	0.7815
1-CH_3	-0.1403	1.4860	0.4734	0.5642	0.6452	1.0153	0.3255	0.6117	0.6922	0.6843	1.0227	0.8608
1-CN	-0.1484	1.2657	0.2532	0.3439	0.4249	0.7950	0.1052	0.3914	0.4719	0.4640	0.8024	0.6406
1-NO_2	-0.1755	0.5263	-0.4862	-0.3954	-0.3145	0.0557	-0.6342	-0.3479	-0.2675	-0.2754	0.0630	-0.0988
2-NH_2	-0.1372	1.5695	0.5570	0.6478	0.7287	1.0989	0.4090	0.6953	0.7758	0.7679	1.1063	0.9444
2-OH	-0.1426	1.4209	0.4084	0.4991	0.5801	0.9502	0.2604	0.5466	0.6271	0.6192	0.9576	0.7958
2-CH_3	-0.1398	1.4980	0.4855	0.5763	0.6572	1.0274	0.3375	0.6238	0.7043	0.6964	1.0348	0.8729
2-CN	-0.1489	1.2509	0.2384	0.3291	0.4101	0.7802	0.0904	0.3766	0.4571	0.4492	0.7876	0.6258
2-NO_2	-0.1589	0.9798	-0.0328	0.0580	0.1390	0.5091	-0.1807	0.1055	0.1860	0.1781	0.5165	0.3546
1,3,5,7-NH_2	-0.0969	2.6668	1.6543	1.7451	1.8260	2.1962	1.5063	1.7926	1.8730	1.8651	2.2035	2.0417
1,3,5,7-OH	-0.1083	2.3558	1.3432	1.4340	1.5150	1.8851	1.1953	1.4815	1.5620	1.5541	1.8925	1.7306
1,3,5,7-CH_3	-0.1133	2.2207	1.2081	1.2989	1.3798	1.7500	1.0602	1.3464	1.4269	1.4190	1.7574	1.5955
1,3,5,7-CN	-0.1555	1.0721	0.0596	0.1503	0.2313	0.6014	-0.0884	0.1978	0.2783	0.2704	0.6088	0.4470
1,3,5,7-NO_2	-0.1626	0.8770	-0.1356	-0.0448	0.0362	0.4063	-0.2835	0.0027	0.0832	0.0753	0.4137	0.2518

Table B.18: ΔE_2 (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	Oxidised AH_2Q	1,3,5,7-NH_2	1,3,5,7-OH	1,3,5,7-CH_3	1,3,5,7-CN	1,3,5,7-NO_2
Reduced quinone	$\Delta E_{\mathrm{absolute}}$ (E_h)	0.1539	0.1752	0.1757	0.2246	0.2300
Benzoquinones						
H	-0.1411	0.3476	0.9279	0.9410	2.2718	2.4182
2-NH_2	-0.2974	-3.9032	-3.3229	-3.3098	-1.9790	-1.8326
2-OH	-0.1391	0.4031	0.9834	0.9964	2.3273	2.4737
2-CH_3	-0.2825	-3.4977	-2.9174	-2.9043	-1.5735	-1.4271
2-CN	-0.2497	-2.6077	-2.0274	-2.0143	-0.6834	-0.5371
2-NO_2	-0.2431	-2.4264	-1.8461	-1.8330	-0.5021	-0.3558
2,5-NH_2	-0.3234	-4.6111	-4.0308	-4.0177	-2.6869	-2.5405
2,5-OH	-0.2936	-3.8007	-3.2204	-3.2074	-1.8765	-1.7301
2,5-CH_3	-0.2873	-3.6296	-3.0493	-3.0363	-1.7054	-1.5590
2,5-CN	-0.2286	-2.0316	-1.4513	-1.4382	-0.1074	0.0390
2,5-NO_2	-0.2203	-1.8070	-1.2266	-1.2136	0.1173	0.2636
Naphthoquinones						
H	-0.1307	0.6328	1.2131	1.2262	2.5570	2.7034
2-NH_2	-0.1288	0.6829	1.2632	1.2763	2.6071	2.7535
2-OH	-0.1379	0.4362	1.0165	1.0295	2.3604	2.5067
2-CH_3	-0.1404	0.3686	0.9489	0.9620	2.2928	2.4392
2-CN	-0.1601	-0.1673	0.4130	0.4260	1.7569	1.9033
2-NO_2	-0.1843	-0.8259	-0.2456	-0.2325	1.0984	1.2447
5-NH_2	-0.1421	0.3217	0.9020	0.9151	2.2459	2.3923
5-OH	-0.1437	0.2772	0.8575	0.8706	2.2015	2.3478
5-CH_3	-0.1403	0.3700	0.9503	0.9634	2.2942	2.4406
5-CN	-0.1514	0.0686	0.6490	0.6620	1.9929	2.1392
5-NO_2	-0.1778	-0.6505	-0.0702	-0.0572	1.2737	1.4201
6-NH_2	-0.1353	0.5067	1.0870	1.1001	2.4309	2.5773
6-OH	-0.1453	0.2339	0.8142	0.8273	2.1581	2.3045
6-CH_3	-0.1414	0.3405	0.9208	0.9338	2.2647	2.4111
6-CN	-0.1544	-0.0142	0.5661	0.5791	1.9100	2.0564
6-NO_2	-0.1615	-0.2075	0.3728	0.3859	1.7168	1.8631
2,5,7-NH_2	-0.0970	1.5480	2.1283	2.1414	3.4723	3.6186
2,5,7-OH	-0.1125	1.1268	1.7071	1.7202	3.0511	3.1974
2,5,7-CH_3	-0.1193	0.9411	1.5214	1.5344	2.8653	3.0117
2,5,7-CN	-0.1653	-0.3095	0.2708	0.2839	1.6148	1.7611
2,5,7-NO_2	-0.1721	-0.4957	0.0846	0.0977	1.4286	1.5749
2,5,8-NH_2	-0.0958	1.5804	2.1607	2.1738	3.5047	3.6510
2,5,8-OH	-0.1104	1.1850	1.7653	1.7784	3.1092	3.2556
2,5,8-CH_3	-0.1183	0.9678	1.5481	1.5612	2.8921	3.0384
2,5,8-CN	-0.1624	-0.2301	0.3502	0.3632	1.6941	1.8405
2,5,8-NO_2	-0.1675	-0.3692	0.2111	0.2242	1.5550	1.7014
2,6,8-NH_2	-0.0969	1.5523	2.1326	2.1457	3.4765	3.6229
2,6,8-OH	-0.1109	1.1700	1.7503	1.7633	3.0942	3.2406
2,6,8-CH_3	-0.1188	0.9557	1.5360	1.5491	2.8799	3.0263
2,6,8-CN	-0.1622	-0.2243	0.3560	0.3691	1.6999	1.8463
2,6,8-NO_2	-0.1676	-0.3735	0.2068	0.2199	1.5507	1.6971
Anthraquinones						
H	-0.1320	0.5957	1.1760	1.1891	2.5199	2.6663
1-NH_2	-0.1410	0.3506	0.9309	0.9440	2.2748	2.4212
1-OH	-0.1432	0.2923	0.8726	0.8856	2.2165	2.3629
1-CH_3	-0.1403	0.3716	0.9519	0.9650	2.2958	2.4422
1-CN	-0.1484	0.1513	0.7317	0.7447	2.0756	2.2219
1-NO_2	-0.1755	-0.5880	-0.0077	0.0053	1.3362	1.4826
2-NH_2	-0.1372	0.4552	1.0355	1.0486	2.3794	2.5258
2-OH	-0.1426	0.3065	0.8868	0.8999	2.2308	2.3771
2-CH_3	-0.1398	0.3837	0.9640	0.9771	2.3079	2.4543
2-CN	-0.1489	0.1366	0.7169	0.7299	2.0608	2.2072
2-NO_2	-0.1589	-0.1346	0.4457	0.4588	1.7896	1.9360
1,3,5,7-NH_2	-0.0969	1.5525	2.1328	2.1458	3.4767	3.6231
1,3,5,7-OH	-0.1083	1.2414	1.8217	1.8348	3.1656	3.3120
1,3,5,7-CH_3	-0.1133	1.1063	1.6866	1.6997	3.0305	3.1769
1,3,5,7-CN	-0.1555	-0.0423	0.5380	0.5511	1.8820	2.0283
1,3,5,7-NO_2	-0.1626	-0.2374	0.3429	0.3560	1.6868	1.8332

B.3 Photorechargeability index

The photo-recharging efficiency index, P, is defined in this work as:

$$P = f_{\mathrm{SQ}} \times \Delta E_{\mathrm{stored}} \tag{B.1}$$

where f_{SQ} is the fractional Shockley-Queisser efficiency[30,31] of the least efficient charging step in the charging reaction, and $\Delta E_{\mathrm{stored}}$ is the energy stored by the charging reaction.

Table B.19: P (eV) for coupled redox reactions involving oxidation of benzohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised BH_2Q	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	2,5-NH_2	2,5-OH	2,5-CH_3	2,5-CN	2,5-NO_2
Reduced quinone											
Benzoquinones											
H	—	—	—	—	0.0085	0.0128	—	—	—	0.0084	0.0079
2-NH_2	0	—	0	0	0	0	—	—	0	0	0
2-OH	0.1028	—	—	0.0209	0.0346	0.0309	—	—	—	0.0173	0.0147
2-CH_3	0	—	—	—	0	0	—	—	—	0	0
2-CN	—	—	—	—	—	0	—	—	—	0.0052	0.0414
2-NO_2	—	—	—	—	—	—	—	—	—	0.0047	0.0493
2,5-NH_2	0	0	0	0	0	0	—	0	0	0	0
2,5-OH	0	0	0	0	0	0	—	—	0	0	0
2,5-CH_3	0	—	0	0	0	0	—	—	—	0	0
2,5-CN	—	—	—	—	—	—	—	—	—	—	0.0552
2,5-NO_2	—	—	—	—	—	—	—	—	—	—	—
Naphthoquinones											
H	0.0883	0	0.0069	0.0196	0.0226	0.0173	0	0	0.0061	0.0089	0.0053
2-NH_2	0.2070	0.1423	0.1036	0.0948	0.0384	0.0344	0	0.0660	0.1028	0.0170	0.0091
2-OH	0.2210	0.1283	0.0970	0.1011	0.0697	0.0567	0	0.0433	0.1009	0.0308	0.0173
2-CH_3	0.1545	0.1076	0.0871	0.0972	0.0736	0.0612	0	0.0228	0.0897	0.0283	0.0218
2-CN	0	0	0	0	0.0019	0.0190	—	0	0	0.0172	0.0252
2-NO_2	0.0926	0	0	0.0273	0.1499	0.1695	—	0	0	0.1433	0.1617
5-NH_2	0.1900	0.1296	0.1035	0.1137	0.0783	0.0647	0	0.0397	0.1065	0.0364	0.0228
5-OH	0.1618	0.0999	0.0889	0.1001	0.0811	0.0681	0	0.0142	0.0876	0.0333	0.0271
5-CH_3	0.1535	0.0940	0.0778	0.0893	0.0701	0.0586	0	0.0116	0.0800	0.0271	0.0211
5-CN	0.1563	0.0501	0.0580	0.0830	0.1059	0.0851	0	0	0.0579	0.0514	0.0342
5-NO_2	0.1603	0.0048	0.0305	0.0727	0.1815	0.1925	—	0	0.0278	0.1628	0.1610
6-NH_2	0.1474	0.0978	0.0760	0.0815	0.0550	0.0426	0	0.0209	0.0750	0.0237	0.0162
6-OH	0.1551	0.0923	0.0842	0.0980	0.0883	0.0767	0	0.0056	0.0829	0.0413	0.0264
6-CH_3	0.1465	0.0848	0.0735	0.0875	0.0673	0.0565	0	0.0029	0.0724	0.0320	0.0205
6-CN	0.1453	0.0293	0.0444	0.0723	0.1037	0.0966	0	0	0.0436	0.0645	0.0509
6-NO_2	0.1577	0.0035	0.0253	0.0622	0.1155	0.1167	0	0	0.0239	0.0851	0.0643
2,5,7-NH_2	0.0415	0.0420	0.0154	0.0129	0.0014	0.0002	0.0148	0.0150	0.0196	0	0
2,5,7-OH	0.0727	0.0416	0.0234	0.0212	0.0081	0.0059	0	0.0053	0.0230	0.0011	0
2,5,7-CH_3	0.1019	0.0373	0.0229	0.0243	0.0135	0.0113	0	0	0.0258	0.0029	0.0012
2,5,7-CN	0.0120	0	0	0	0.0317	0.0473	—	0	0	0.0440	0.0457
2,5,7-NO_2	0.0101	0	0	0	0.0361	0.0575	—	0	0	0.0522	0.0625
2,5,8-NH_2	0.0477	0.0517	0.0187	0.0153	0.0002	0	0.0436	0.0201	0.0186	0	0
2,5,8-OH	0.0721	0.0508	0.0255	0.0201	0.0091	0.0034	0	0.0122	0.0252	0.0002	0
2,5,8-CH_3	0.0947	0.0450	0.0278	0.0280	0.0146	0.0087	0	0.0025	0.0274	0.0031	0.0012
2,5,8-CN	0.0356	0	0	0	0.0424	0.0530	—	0	0	0.0415	0.0448
2,5,8-NO_2	0	0	0	0	0	0.0006	—	0	0	0.0073	0.0260
2,6,8-NH_2	0.0505	0.0561	0.0201	0.0164	0.0017	0.0002	0.0565	0.0224	0.0257	0	0
2,6,8-OH	0.0853	0.0538	0.0267	0.0210	0.0093	0.0067	0	0.0162	0.0265	0.0012	0
2,6,8-CH_3	0.0890	0.0402	0.0242	0.0253	0.0138	0.0115	0	0	0.0274	0.0030	0.0012
2,6,8-CN	0.0154	0	0	0	0.0295	0.0436	—	0	0	0.0351	0.0403
2,6,8-NO_2	0	0	0	0	0	0	—	0	0	0	0.0189
Anthraquinones											
H	0.1699	0.1700	0.1181	0.1099	0.0512	0.0435	0	0.0827	0.1173	0.0240	0.0145
1-NH_2	0.2666	0.3707	0.2780	0.2519	0.1424	0.1123	0.1639	0.2462	0.2768	0.0621	0.0366
1-OH	0.2350	0.3342	0.2459	0.2596	0.1345	0.1064	0.1374	0.2334	0.2656	0.0483	0.0349
1-CH_3	0.1655	0.0423	0.0466	0.0624	0.0581	0.0497	—	0	0.0475	0.0232	0.0185
1-CN	0.2826	0.2860	0.2335	0.2321	0.1628	0.1393	0.0282	0.1758	0.2390	0.0788	0.0463
1-NO_2	0.4247	0.2156	0.3065	0.3494	0.4009	0.3803	0.0014	0.1781	0.3074	0.3019	0.2559
2-NH_2	0.1831	0.3060	0.2126	0.2079	0.1002	0.0738	0.1370	0.2010	0.2233	0.0403	0.0257
2-OH	0.2248	0.3006	0.2212	0.2217	0.1108	0.0870	0.1123	0.2088	0.2305	0.0465	0.0337
2-CH_3	0.3130	0.3114	0.2301	0.2204	0.1103	0.0866	0.0854	0.1950	0.2290	0.0463	0.0336
2-CN	0.3783	0.2836	0.2362	0.2370	0.1765	0.1378	0.0145	0.1710	0.2413	0.0780	0.0560
2-NO_2	0.1824	0.2281	0.1722	0.1891	0.1062	0.0854	0.0072	0.1400	0.1857	0.0390	0.0288
1,3,5,7-NH_2	0.0516	0.0756	0.0268	0.0213	0.0021	0.0003	0.1142	0.0326	0.0267	0	0
1,3,5,7-OH	0.0840	0.0988	0.0418	0.0300	0.0089	0.0050	0.0476	0.0410	0.0416	0.0002	0
1,3,5,7-CH_3	0.1112	0.1385	0.0591	0.0459	0.0135	0.0094	0.0492	0.0614	0.0587	0.0017	0
1,3,5,7-CN	0.2517	0.0991	0.1096	0.1320	0.1372	0.1233	0	0.0106	0.1100	0.0813	0.0615
1,3,5,7-NO_2	0.1947	0.0216	0.0499	0.0861	0.1354	0.1286	—	0	0.0486	0.0932	0.0804

Table B.20: P (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised {NH2Q}	H	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2	5-NH_2	5-OH	5-CH_3	5-CN	5-NO_2
Reduced quinone											
Benzoquinones											
H	0	0	0	0	0.0304	0	0	0	0	0	0
2-NH_2	—	—	—	—	—	—	—	—	—	—	—
2-OH	0	0	0	0	0.1455	0.0145	0	0	0	0	0
2-CH_3	—	—	—	—	—	—	—	—	—	—	—
2-CN	—	—	—	—	—	—	—	—	—	—	—
2-NO_2	—	—	—	—	—	—	—	—	—	—	—
2,5-NH_2	—	—	—	—	—	—	—	—	—	—	—
2,5-OH	—	—	—	—	—	—	—	—	—	—	—
2,5-CH_3	—	—	—	—	—	—	—	—	—	—	—
2,5-CN	—	—	—	—	—	—	—	—	—	—	—
2,5-NO_2	—	—	—	—	—	—	—	—	—	—	—
Naphthoquinones											
H	0	0	0	0	0.1174	0.0213	0	0	0	0	0
2-NH_2	0.1468	0	0.0626	0.0885	0.2367	0.1549	0.0782	0.1115	0.1058	0.1145	0.2123
2-OH	0.1306	0	0	0.0334	0.2601	0.1492	0.0120	0.0472	0.0498	0.0878	0.1429
2-CH_3	0.0841	0	0	0	0.1815	0.1013	0	0.0137	0.0146	0.0495	0.1098
2-CN	0	—	0	0	0	0	—	0	0	0	0
2-NO_2	0	—	—	—	0.0830	0	—	—	—	0	—
5-NH_2	0.1113	0	0	0.0199	0.2275	0.1275	0	0.0332	0.0361	0.0718	0.1201
5-OH	0.0809	0	0	0	0.1897	0.1002	0	0	0.0019	0.0432	0.0818
5-CH_3	0.0768	0	0	0	0.1808	0.0917	0	0	0	0.0405	0.0950
5-CN	0.0473	0	0	0	0.1918	0.0715	0	0	0	0	0.0256
5-NO_2	0.0113	—	—	0	0.1530	0.0288	—	—	0	0	—
6-NH_2	0.0820	0	0	0.0017	0.1737	0.0983	0	0.0156	0.0161	0.0490	0.1152
6-OH	0.0754	0	0	0	0.1901	0.0926	0	0	0	0.0362	0.0691
6-CH_3	0.0710	0	0	0	0.1809	0.0874	0	0	0	0.0330	0.0806
6-CN	0.0311	0	0	0	0.1800	0.0578	0	0	0	0	0.0108
6-NO_2	0.0107	—	0	0	0.1947	0.0426	0	0	0	0	0
2,5,7-NH_2	0.0506	0.0586	0.0806	0.0814	0.0826	0.0650	0.0956	0.0985	0.0835	0.0553	0.1829
2,5,7-OH	0.0518	0	0	0	0.1322	0.0703	0	0.0043	0.0052	0.0317	0.0969
2,5,7-CH_3	0.0406	0	0	0	0.1162	0.0532	0	0	0	0.0143	0.0619
2,5,7-CN	0	—	0	0	0.0446	0	0	0	0	0	0
2,5,7-NO_2	0	—	0	0	0.0379	0	—	0	0	0	—
2,5,8-NH_2	0.0621	0.0997	0.1099	0.1072	0.0800	0.0782	0.1338	0.1280	0.1070	0.0607	0.2088
2,5,8-OH	0.0582	0	0	0.0225	0.1268	0.0824	0.0089	0.0345	0.0320	0.0444	0.1268
2,5,8-CH_3	0.0512	0	0	0	0.1255	0.0591	0	0	0	0.0240	0.0790
2,5,8-CN	0	—	0	0	0.0704	0	0	0	0	0	0
2,5,8-NO_2	0	—	0	0	0	0	0	0	0	0	0
2,6,8-NH_2	0.0672	0.1133	0.1197	0.1133	0.0843	0.0728	0.1588	0.1435	0.1280	0.0666	0.2062
2,6,8-OH	0.0615	0	0.0053	0.0291	0.1300	0.0862	0.0171	0.0415	0.0381	0.0515	0.1346
2,6,8-CH_3	0.0436	0	0	0	0.1188	0.0559	0	0	0	0.0174	0.0674
2,6,8-CN	0	—	0	0	0.0502	0	0	0	0	0	0
2,6,8-NO_2	0	—	0	0	0	0	0	0	0	0	0
Anthraquinones											
H	0.1251	0.0128	0.0705	0.0911	0.1967	0.1339	0.0969	0.1178	0.1088	0.1016	0.2084
1-NH_2	0.2455	0.1056	0.2484	0.2583	0.3183	0.2514	0.2569	0.3037	0.2818	0.2235	0.3909
1-OH	0.2148	0.0737	0.2080	0.2191	0.2662	0.2080	0.1992	0.2635	0.2419	0.1938	0.3161
1-CH_3	0.0561	0	0	0	0.2233	0.0905	0	0	0	0.0056	0.0312
1-CN	0.2216	0.0169	0.1052	0.1624	0.3275	0.2311	0.1106	0.1605	0.1793	0.1853	0.2125
1-NO_2	0.2160	—	—	0.0142	0.3630	0.2258	—	0.0085	0.0283	0.1472	—
2-NH_2	0.1810	0.1072	0.1932	0.1981	0.2500	0.1836	0.2397	0.2460	0.2159	0.1655	0.3282
2-OH	0.1913	0.0673	0.1798	0.1898	0.2391	0.1844	0.1841	0.2337	0.2121	0.1624	0.3085
2-CH_3	0.2656	0.0781	0.2011	0.2315	0.3613	0.2703	0.2103	0.2635	0.2549	0.2321	0.3413
2-CN	0.2766	0.0147	0.1006	0.1555	0.4219	0.2952	0.1047	0.1513	0.1738	0.2264	0.2059
2-NO_2	0.1478	—	0.0538	0.0944	0.2099	0.1481	0.0420	0.0896	0.1186	0.1234	0.0942
1,3,5,7-NH_2	0.0624	0.1734	0.1570	0.1329	0.0660	0.0517	0.2464	0.1768	0.1380	0.0685	0.2199
1,3,5,7-OH	0.0776	0.0836	0.1008	0.1016	0.1037	0.0732	0.1596	0.1389	0.1157	0.0745	0.2017
1,3,5,7-CH_3	0.1099	0.0901	0.1134	0.1203	0.1368	0.1083	0.1681	0.1548	0.1352	0.0913	0.2273
1,3,5,7-CN	0.1111	0	0	0	0.2913	0.1420	0	0	0	0.0548	0.0479
1,3,5,7-NO_2	0.0356	—	0	0	0.2328	0.0660	0	0	0	0	0.0045

Table B.21: P (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised NH_2Q	6-NH_2	6-OH	6-CH_3	6-CN	6-NO_2	2,5,7-NH_2	2,5,7-OH	2,5,7-CH_3	2,5,7-CN	2,5,7-NO_2
Reduced quinone										
Benzoquinones										
H	0	0	0	0	0	0	0	0	0	0
2-NH_2	—	—	—	—	—	—	—	—	—	—
2-OH	0	0	0	0	0	0	0	0	0.0290	0.0219
2-CH_3	—	—	—	—	—	—	—	—	—	—
2-CN	—	—	—	—	—	—	—	—	—	—
2-NO_2	—	—	—	—	—	—	—	—	—	—
2,5-NH_2	—	—	—	—	—	—	—	—	—	—
2,5-OH	—	—	—	—	—	—	—	—	—	—
2,5-CH_3	—	—	—	—	—	—	—	—	—	—
2,5-CN	—	—	—	—	—	—	—	—	0	0
2,5-NO_2	—	—	—	—	—	—	—	—	0	0
Naphthoquinones										
H	0	0	0	0	0	0	0	0	0.0207	0.0109
2-NH_2	0.0985	0.1160	0.1126	0.1237	0.1601	0	0.0887	0.1147	0.0435	0.0233
2-OH	0.0296	0.0605	0.0613	0.1021	0.1357	0	0.0399	0.0752	0.0601	0.0361
2-CH_3	0	0.0238	0.0254	0.0610	0.0884	0	0.0071	0.0379	0.0321	0.0172
2-CN	—	0	0	0	0	—	0	0	0	0
2-NO_2	—	—	—	0	0	—	—	0	0.0713	0.0575
5-NH_2	0.0144	0.0458	0.0466	0.0849	0.1151	0	0.0263	0.0592	0.0424	0.0271
5-OH	0	0.0112	0.0135	0.0561	0.0829	0	0	0.0278	0.0375	0.0196
5-CH_3	0	0.0091	0.0114	0.0529	0.0792	0	0	0.0257	0.0303	0.0195
5-CN	0	0	0	0.0173	0.0423	0	0	0	0.0456	0.0290
5-NO_2	—	0	0	0	0.0019	—	0	0	0.1103	0.0868
6-NH_2	0	0.0252	0.0265	0.0598	0.0872	0	0.0085	0.0375	0.0252	0.0173
6-OH	0	0	0.0028	0.0499	0.0758	0	0	0.0185	0.0358	0.0188
6-CH_3	0	0	0	0.0462	0.0718	0	0	0.0156	0.0288	0.0186
6-CN	0	0	0	0	0.0236	0	0	0	0.0470	0.0260
6-NO_2	0	0	0	0	0	—	0	0	0.0655	0.0461
2,5,7-NH_2	0.1156	0.0823	0.0835	0.0515	0.0854	0	0.0753	0.0778	0.0013	0.0002
2,5,7-OH	0	0.0115	0.0139	0.0391	0.0633	0	0	0.0234	0.0095	0.0045
2,5,7-CH_3	0	0	0	0.0234	0.0438	0	0	0	0.0142	0.0082
2,5,7-CN	0	0	0	0	0	—	0	0	0	0.0007
2,5,7-NO_2	—	0	0	0	0	—	0	0	0	0
2,5,8-NH_2	0.1568	0.1111	0.1123	0.0648	0.1054	0.0528	0.0886	0.0933	0.0015	0.0002
2,5,8-OH	0.0265	0.0358	0.0391	0.0532	0.0813	0	0.0242	0.0456	0.0078	0.0051
2,5,8-CH_3	0	0.0006	0.0027	0.0319	0.0516	0	0	0.0136	0.0122	0.0065
2,5,8-CN	0	0	0	0	0	—	0	0	0.0126	0.0101
2,5,8-NO_2	—	0	0	0	0	—	0	0	0	0
2,6,8-NH_2	0.1707	0.1239	0.1252	0.0707	0.1013	0.0723	0.0908	0.1033	0.0016	0.0002
2,6,8-OH	0.0347	0.0416	0.0451	0.0570	0.0861	0	0.0309	0.0509	0.0113	0.0053
2,6,8-CH_3	0	0	0	0.0263	0.0453	0	0	0.0039	0.0146	0.0085
2,6,8-CN	0	0	0	0	0	—	0	0	0.0017	0.0020
2,6,8-NO_2	—	0	0	0	0	—	0	0	0	0
Anthraquinones										
H	0.1104	0.1167	0.1107	0.1068	0.1390	0	0.0876	0.1071	0.0242	0.0140
1-NH_2	0.2422	0.2902	0.2771	0.2252	0.2821	0.0825	0.2358	0.2568	0.0432	0.0281
1-OH	0.2033	0.2500	0.2360	0.1955	0.2400	0.0543	0.1974	0.2172	0.0406	0.0195
1-CH_3	0	0	0	0.0252	0.0524	0	0	0	0.0540	0.0351
1-CN	0.1085	0.1944	0.1905	0.1952	0.2377	0.0005	0.1625	0.1919	0.0639	0.0407
1-NO_2	—	0.0426	0.0366	0.1750	0.1336	—	0.0418	0.0705	0.2192	0.1826
2-NH_2	0.2502	0.2230	0.2124	0.1648	0.2099	0.0752	0.1787	0.1871	0.0264	0.0140
2-OH	0.1854	0.2199	0.2059	0.1730	0.2157	0.0418	0.1743	0.1935	0.0323	0.0186
2-CH_3	0.2056	0.2644	0.2549	0.2400	0.2882	0.0495	0.2242	0.2499	0.0740	0.0387
2-CN	0.1006	0.1852	0.1864	0.2431	0.2830	0	0.1724	0.2182	0.1448	0.0861
2-NO_2	0.0368	0.1290	0.1298	0.1285	0.1631	0	0.1086	0.1313	0.0313	0.0150
1,3,5,7-NH_2	0.2052	0.1547	0.1274	0.0582	0.0884	0.1450	0.0936	0.1022	0.0003	0
1,3,5,7-OH	0.1494	0.1206	0.1151	0.0695	0.0978	0.0334	0.0930	0.0929	0.0081	0.0014
1,3,5,7-CH_3	0.1645	0.1410	0.1308	0.0981	0.1370	0.0304	0.1080	0.1201	0.0122	0.0042
1,3,5,7-CN	0	0.0037	0.0058	0.0749	0.0966	0	0	0.0245	0.1076	0.0754
1,3,5,7-NO_2	0	0	0	0	0.0203	—	0	0	0.0966	0.0766

Table B.22: P (eV) for coupled redox reactions involving oxidation of naphthohydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised NH_2Q	2,5,8-NH_2	2,5,8-OH	2,5,8-CH_3	2,5,8-CN	2,5,8-NO_2	2,6,8-NH_2	2,6,8-OH	2,6,8-CH_3	2,6,8-CN	2,6,8-NO_2
Reduced quinone										
Benzoquinones										
H	0	0	0	0	0.0146	0	0	0	0	0.0193
2-NH_2	—	—	—	—	—	—	—	—	—	—
2-OH	0	0	0	0.0276	0.0362	0	0	0	0.0284	0.0403
2-CH_3	—	—	—	—	—	—	—	—	—	—
2-CN	—	—	—	—	—	—	—	—	—	—
2-NO_2	—	—	—	—	—	—	—	—	—	—
2,5-NH_2	—	—	—	—	—	—	—	—	—	—
2,5-OH	—	—	—	—	—	—	—	—	—	—
2,5-CH_3	—	—	—	—	—	—	—	—	—	—
2,5-CN	—	—	—	0	0	—	—	—	0	0.0027
2,5-NO_2	—	—	—	0	0	—	—	—	0	0
Naphthoquinones										
H	0	0	0	0.0175	0.0210	0	0	0	0.0203	0.0191
2-NH_2	0	0.0633	0.1039	0.0409	0.0343	0	0.0512	0.1126	0.0431	0.0301
2-OH	0	0.0025	0.0558	0.0557	0.0566	0	0	0.0694	0.0595	0.0489
2-CH_3	0	0	0.0208	0.0295	0.0270	0	0	0.0329	0.0318	0.0288
2-CN	—	0	0	0	0.0209	—	0	0	0	0.0332
2-NO_2	—	—	0	0.0570	0.1065	—	0	0	0.0695	0.1132
5-NH_2	0	0	0.0420	0.0461	0.0446	0	0	0.0546	0.0420	0.0370
5-OH	0	0	0.0096	0.0343	0.0317	0	0	0.0231	0.0370	0.0278
5-CH_3	0	0	0.0078	0.0277	0.0259	0	0	0.0210	0.0299	0.0277
5-CN	—	0	0	0.0405	0.0485	0	0	0	0.0449	0.0447
5-NO_2	—	0	0	0.0948	0.1460	—	0	0	0.1083	0.1531
6-NH_2	0	0	0.0220	0.0232	0.0272	0	0	0.0336	0.0250	0.0241
6-OH	0	0	0	0.0326	0.0307	0	0	0.0134	0.0354	0.0329
6-CH_3	0	0	0	0.0322	0.0304	0	0	0.0104	0.0285	0.0267
6-CN	—	0	0	0.0412	0.0450	0	0	0	0.0463	0.0491
6-NO_2	—	0	0	0.0598	0.0871	—	0	0	0.0643	0.0874
2,5,7-NH_2	0	0.0667	0.0820	0.0012	0.0002	0	0.0468	0.0689	0.0013	0.0002
2,5,7-OH	0	0	0.0106	0.0087	0.0090	0	0	0.0188	0.0094	0.0097
2,5,7-CH_3	0	0	0	0.0128	0.0113	0	0	0	0.0140	0.0121
2,5,7-CN	—	0	0	0	0.0443	—	0	0	0	0.0534
2,5,7-NO_2	—	0	0	0	0.0482	—	0	0	0	0.0588
2,5,8-NH_2	0	0.0933	0.0943	0.0014	0.0002	0	0.0713	0.0913	0.0015	0.0002
2,5,8-OH	0	0	0.0340	0.0101	0.0065	0	0	0.0401	0.0078	0.0069
2,5,8-CH_3	0	0	0	0.0142	0.0121	0	0	0.0102	0.0154	0.0129
2,5,8-CN	—	0	0	0	0.0525	—	0	0	0.0110	0.0602
2,5,8-NO_2	—	0	0	0	0	—	0	0	0	0.0116
2,6,8-NH_2	0.0236	0.1071	0.1053	0.0015	0.0002	0	0.0822	0.1013	0.0016	0.0002
2,6,8-OH	0	0.0066	0.0395	0.0105	0.0067	0	0	0.0452	0.0112	0.0071
2,6,8-CH_3	0	0	0	0.0132	0.0115	0	0	0	0.0144	0.0124
2,6,8-CN	—	0	0	0	0.0457	—	0	0	0	0.0547
2,6,8-NO_2	—	0	0	0	0	—	0	0	0	0
Anthraquinones										
H	0	0.0700	0.1020	0.0274	0.0231	0	0.0566	0.1068	0.0240	0.0179
1-NH_2	0.0161	0.2443	0.2546	0.0506	0.0413	0.0194	0.2152	0.2598	0.0430	0.0335
1-OH	0.0058	0.2025	0.2150	0.0389	0.0306	0.0003	0.1778	0.2201	0.0404	0.0318
1-CH_3	0	0	0	0.0481	0.0572	0	0	0	0.0532	0.0619
1-CN	0	0.1342	0.1794	0.0714	0.0485	0	0.1239	0.1892	0.0635	0.0507
1-NO_2	—	0.0148	0.0496	0.2193	0.2186	—	0.0335	0.0779	0.2178	0.2288
2-NH_2	0.0128	0.1858	0.1959	0.0254	0.0226	0.0014	0.1588	0.1914	0.0263	0.0168
2-OH	0.0014	0.1743	0.1915	0.0309	0.0217	0	0.1547	0.1895	0.0321	0.0225
2-CH_3	0.0012	0.2101	0.2446	0.0708	0.0549	0	0.1909	0.2492	0.0736	0.0571
2-CN	—	0.1285	0.1930	0.1374	0.1196	0	0.1270	0.2116	0.1438	0.1250
2-NO_2	—	0.0809	0.1236	0.0296	0.0245	—	0.0810	0.1313	0.0311	0.0257
1,3,5,7-NH_2	0.1072	0.1346	0.1118	0.0002	0	0.1032	0.1075	0.1008	0.0003	0
1,3,5,7-OH	0	0.0972	0.0998	0.0077	0.0017	0	0.0776	0.1065	0.0081	0.0017
1,3,5,7-CH_3	0	0.1109	0.1161	0.0117	0.0094	0	0.0926	0.1171	0.0122	0.0052
1,3,5,7-CN	—	0	0.0033	0.0982	0.1122	0	0	0.0187	0.1064	0.1201
1,3,5,7-NO_2	—	0	0	0.0888	0.1203	—	0	0	0.0950	0.1229

Table B.23: P (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

Oxidised AH_2Q	H	1-NH_2	1-OH	1-CH_3	1-CN	1-NO_2	2-NH_2	2-OH	2-CH_3	2-CN	2-NO_2
Reduced quinone											
Benzoquinones											
H	0	0	0	0	0	0	0	0	0	0	0
2-NH_2	—	—	—	—	—	—	—	—	—	—	—
2-OH	0	0	0	0	0	0	0	0	0	0	0
2-CH_3	—	—	—	—	—	—	—	—	—	—	—
2-CN	—	—	—	—	—	—	—	—	—	—	—
2-NO_2	—	—	—	—	—	—	—	—	—	—	—
2,5-NH_2	—	—	—	—	—	—	—	—	—	—	—
2,5-OH	—	—	—	—	—	—	—	—	—	—	—
2,5-CH_3	—	—	—	—	—	—	—	—	—	—	—
2,5-CN	—	—	—	—	—	—	—	—	—	—	—
2,5-NO_2	—	—	—	—	—	—	—	—	—	—	—
Naphthoquinones											
H	0	0	0	0	0	0	0	0	0	0	0
2-NH_2	0	0	0	0.1584	0	0	0	0	0	0	0
2-OH	0	0	0	0.0742	0	0	0	0	0	0	0
2-CH_3	0	0	0	0.0417	0	0	0	0	0	0	0
2-CN	0	—	—	—	0	—	—	—	—	0	0
2-NO_2	0	—	—	—	—	—	—	—	—	—	—
5-NH_2	0	0	0	0.0493	0	0	0	0	0	0	0
5-OH	0	0	0	0.0283	0	0	0	0	0	0	0
5-CH_3	0	0	0	0.0325	0	0	0	0	0	0	0
5-CN	0	0	0	0	0	—	0	0	0	0	0
5-NO_2	0	—	—	—	—	—	—	—	—	—	—
6-NH_2	0	0	0	0.0534	0	0	0	0	0	0	0
6-OH	0	0	0	0.0203	0	0	0	0	0	0	0
6-CH_3	0	0	0	0.0232	0	0	0	0	0	0	0
6-CN	0	—	0	0	0	—	0	0	0	0	0
6-NO_2	0	—	—	—	0	—	—	—	—	0	0
2,5,7-NH_2	0.0162	0	0	0.2026	0	0.0146	0	0	0	0.0025	0.0176
2,5,7-OH	0	0	0	0.0606	0	0	0	0	0	0	0
2,5,7-CH_3	0	0	0	0.0226	0	0	0	0	0	0	0
2,5,7-CN	0	—	—	—	0	—	—	—	—	0	0
2,5,7-NO_2	0	—	—	—	0	—	—	—	—	0	—
2,5,8-NH_2	0.0362	0	0	0.2497	0.0340	0.0773	0	0	0	0.0368	0.0577
2,5,8-OH	0	0	0	0.1015	0	0	0	0	0	0	0
2,5,8-CH_3	0	0	0	0.0447	0	0	0	0	0	0	0
2,5,8-CN	0	—	—	—	0	—	—	—	—	0	0
2,5,8-NO_2	0	—	—	—	0	—	—	—	—	0	—
2,6,8-NH_2	0.0452	0	0	0.2677	0.0438	0.1014	0	0.0188	0.0198	0.0463	0.0701
2,6,8-OH	0	0	0	0.1107	0	0	0	0	0	0	0
2,6,8-CH_3	0	0	0	0.0286	0	0	0	0	0	0	0
2,6,8-CN	0	—	—	—	0	—	—	—	—	0	0
2,6,8-NO_2	0	—	—	—	0	—	—	—	—	0	—
Anthraquinones											
H	0	0	0	0.1506	0	0	0	0	0	0	0
1-NH_2	0.1638	0	0.0178	0.2183	0.1171	0.0283	0.0185	0.0396	0.0405	0.1238	0.1243
1-OH	0.1288	0	0	0.1789	0.0832	0.0142	0	0.0138	0.0152	0.0879	0.0946
1-CH_3	0	—	0	0	0	—	—	0	0	0	0
1-CN	0.0552	0	0	0.0794	0	—	0	0	0	0.0043	0.0164
1-NO_2	0.0199	—	—	—	—	—	—	—	—	—	—
2-NH_2	0.1141	0	0.0009	0.2507	0.0749	0.0355	0	0.0194	0.0213	0.0813	0.1093
2-OH	0.1033	0	0	0.1701	0.0600	0.0125	0	0	0.0015	0.0645	0.0765
2-CH_3	0.1248	0	0	0.1993	0.0683	0.0195	0	0	0	0.0737	0.0805
2-CN	0.0515	0	0	0.0724	0	—	0	0	0	0	0.0125
2-NO_2	0.0246	—	—	—	0	—	—	0	0	0	0
1,3,5,7-NH_2	0.0854	0.0916	0.1056	0.3261	0.0842	0.1940	0.1098	0.1066	0.1004	0.0862	0.1176
1,3,5,7-OH	0.0466	0	0	0.2427	0.0207	0.0536	0	0	0	0.0249	0.0434
1,3,5,7-CH_3	0.0503	0	0	0.2568	0.0201	0.0472	0	0	0	0.0245	0.0437
1,3,5,7-CN	0	—	0	0.0052	0	—	0	0	0	0	0
1,3,5,7-NO_2	0	—	—	—	0	—	—	—	—	0	0

Table B.24: P (eV) for coupled redox reactions involving oxidation of anthrahydroquinones (columns) and reduction of benzoquinones, naphthoquinones and anthraquinones (rows)

	1,3,5,7-NH_2	1,3,5,7-OH	1,3,5,7-CH_3	1,3,5,7-CN	1,3,5,7-NO_2
Reduced quinone					
Benzoquinones					
H	0	0	0	0	0
2-NH_2	—	—	—	—	—
2-OH	0	0	0	0	0
2-CH_3	—	—	—	—	—
2-CN	—	—	—	—	—
2-NO_2	—	—	—	—	—
2,5-NH_2	—	—	—	—	—
2,5-OH	—	—	—	—	—
2,5-CH_3	—	—	—	—	—
2,5-CN	—	—	—	—	—
2,5-NO_2	—	—	—	—	0
Naphthoquinones					
H	0	0	0	0	0
2-NH_2	0	0	0	0.0200	0.0326
2-OH	0	0	0	0.0159	0.0336
2-CH_3	0	0	0	0.0041	0.0161
2-CN	—	0	0	0	0
2-NO_2	—	—	—	0	0
5-NH_2	0	0	0	0.0108	0.0264
5-OH	0	0	0	0.0016	0.0160
5-CH_3	0	0	0	0.0010	0.0135
5-CN	—	0	0	0	0.0063
5-NO_2	—	—	—	0	0
6-NH_2	0	0	0	0.0038	0.0140
6-OH	0	0	0	0	0.0138
6-CH_3	0	0	0	0	0.0132
6-CN	—	0	0	0	0.0002
6-NO_2	—	0	0	0	0
2,5,7-NH_2	0	0	0	0.0068	0.0068
2,5,7-OH	0	0	0	0.0014	0.0065
2,5,7-CH_3	0	0	0	0	0.0045
2,5,7-CN	—	0	0	0	0
2,5,7-NO_2	—	—	—	0	0
2,5,8-NH_2	0	0.0161	0.0210	0.0066	0.0056
2,5,8-OH	0	0	0	0.0047	0.0094
2,5,8-CH_3	0	0	0	0	0.0053
2,5,8-CN	—	0	0	0	0
2,5,8-NO_2	—	0	0	0	0
2,6,8-NH_2	0	0.0348	0.0381	0.0074	0.0061
2,6,8-OH	0	0	0	0.0055	0.0101
2,6,8-CH_3	0	0	0	0	0.0050
2,6,8-CN	—	0	0	0	0
2,6,8-NO_2	—	0	0	0	0
Anthraquinones					
H	0	0	0	0.0158	0.0191
1-NH_2	0	0.0858	0.0946	0.0464	0.0465
1-OH	0	0.0469	0.0550	0.0337	0.0425
1-CH_3	—	0	0	0	0.0116
1-CN	0	0	0	0.0434	0.0604
1-NO_2	—	—	—	0.1127	0.1546
2-NH_2	0	0.0537	0.0596	0.0264	0.0273
2-OH	0	0.0281	0.0360	0.0309	0.0309
2-CH_3	0	0.0289	0.0367	0.0595	0.0657
2-CN	—	0	0	0.0840	0.1104
2-NO_2	—	0	0	0.0192	0.0279
1,3,5,7-NH_2	0	0.0984	0.0966	0.0037	0.0044
1,3,5,7-OH	0	0	0.0054	0.0083	0.0079
1,3,5,7-CH_3	0	0	0	0.0109	0.0145
1,3,5,7-CN	—	0	0	0	0.0382
1,3,5,7-NO_2	—	0	0	0	0